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ANALYSIS OF ERROR GROWTH AND STABILITY  
FOR THE NUMERICAL INTEGRATION OF THE  
EQUATIONS OF CHEMICAL KINETICS

By D. E. Magnus and Harold S. Schechter

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## FOREWORD

This study of the error growth and stability of numerical procedures for integrating the equations of chemical kinetics was performed by the General Applied Science Laboratories for the Analysis and Computation Division, National Aeronautics and Space Administration, Langley Research Center under Contract NAS 1-5046. The technical monitor of the project was Mr. George W. Haigler of the Digital Analysis and Programming Branch, NASA. The assistance of Dr. John Evans of the Magnetoplasmdynamics Branch, NASA is acknowledged in the selection of the air chemistry system for the numerical experimentation.

## TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
1.	Introduction	2
2.	Statement of The Problem	6
3.	Derivation of Stable Integration Methods	12
4.	Error Behavior of the Rational Approximation Methods	24
5.	Implementation of the Methods	29
6.	Discussion of Numerical Results	35
7.	Conclusions	42
	Appendix A	43
	Appendix B	46
	References	58
	Figures 1 through 10	59-68

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ABSTRACT

Several stable numerical methods of integration are developed for solving the equations of chemical kinetics. The only limitation upon the integration stepsize is imposed by the truncation error and the residual error introduced by the linearization of the ordinary differential equations of chemical kinetics. However, the limitation is not severe and the stable procedures produce accurate solutions using a stepsize which is large compared to the maximum stable stepsize of standard procedures.

The methods have been applied to the hydrogen-air chemistry system, and for a given problem the amount of machine time was reduced by a factor of 10 to 20 as compared to other methods of integration. Also for dissociating air chemistry, the method produced accurate solutions with a substantial saving in machine time. The numerical results for these two chemistry systems are reported herein.

## 1. INTRODUCTION

A chemical reaction involving  $n$  species can be represented by  $n$ -coupled non-linear ordinary differential equations (ODE). In the simplest form the independent variable can be taken as time, and given the appropriate  $n$  initial conditions at some time,  $t_0$ , the mathematical model is properly posed for integration. A variety of standard numerical procedures can be used to integrate these equations, but unfortunately these procedures (Runge-Kutta, predictor-corrector, etc.) exhibit unstable behavior for stepsizes which are very small compared to the domain of integration,  $(t_0, t_f)$ . Consequently, large amounts of machine time may be required to integrate the equations over reasonable domains.

In classical investigations of techniques for integrating ordinary differential equations, the problem of instability is discussed from the viewpoint of the solution behavior as the step-size,  $h$ , approaches zero. The solution of the finite difference equations at  $h=0$ , should not have extraneous solutions which will dominate the desired results; multistep procedures satisfying this requirement are termed strongly stable. However, the unstable behavior of the equations of chemical kinetics is of a different type involving the solution behavior as the stepsize is increased. Since the truncation error will tend to increase in some well-behaved manner as stepsize increases, the numerical solution should "smoothly" depart from the exact solution as the stepsize is increased. When integrating the chemical kinetic equations by standard numerical

methods, the smooth departure exists only to some maximum stable stepsize  $h_s$  which is inversely proportional to the Lipschitz constant of the system. Above this value of stepsize, the numerical solution departs radically from the true solution. Numerical techniques exhibiting such behavior are termed partially unstable in this report. Although the standard single and multi-step integration methods (such as Euler, Adams-Moulton, Runge-Kutta, etc.) are well-suited to a variety of problem areas, the methods are partially unstable and not practical for integrating ODE with large Lipschitz constants as found in the equations of chemical kinetics. (Other problems from physics have the same characteristics; for example, control system problems have a similar behavior as indicated in the introduction of Ref. 1.)

In this report, a class of numerical procedures which are stable are described and investigated for their error behavior. In Section 3, the derivation of these numerical procedures is described from several points of view. The numerical integration formulas, which are termed as rational approximation methods, are initially derived using "trial family techniques" wherein the functions are polynomials. The methods are then interpreted using analogies with more familiar integration approximations, and lastly this whole class of integrators is developed from the viewpoint of rational approximation of the exponential function. This latter approach is conveniently described in terms of the Padé series and

represents the "best" unconditionally stable procedures.

The procedures under discussion are directly applicable to a system of linear ordinary differential equations, which of course have an exponential form of solution. In Section 4, the truncation and propagated errors associated with several rational approximation methods are described and compared for such linear differential equations. The same integration methods may be applied to systems of non-linear differential equations for chemical kinetics by introducing an additional operation; namely, the non-linear differential equations are linearized by a straightforward application of Taylor's Series for  $n$  variables. By linearizing the equations two additional problems arise:

(1) Since the Taylor's Series is truncated after the second term, a residual error is introduced and its effect upon the numerical solution must be included in any numerical analysis study and interpretation of results.

(2) The linear form of the equations must be recomputed at each step of the numerical calculation.

In Section 4, the residual error has been included in the propagated error expression, and to illustrate the importance of residual error upon practical problems the results from two different chemistry systems are reported in Section 6. First, the error behavior results from a detailed study of the hydrogen oxygen com-

bustion process are given. Then the chemical reactions in a dissociating air system behind a bow shock are reported upon. For the sake of simplicity, the only charged particles in the air system are  $\text{NO}^+$  and  $\text{e}^-$ . The effect of stepsize on the propagated error is illustrated, and numerical comparisons are made with results from the Runge-Kutta procedure.

The rational approximation method is not limited in stepsize because of stability requirements and large steps are possible without introducing excessive error. However, because the procedure requires the recomputation of the linear form at each step, the evaluation of the procedure against standard methods must include more than just considerations of stepsize. The evaluation must be made with respect to over-all time on the computer for a given problem. Such results can be obtained by making a detailed count of operations or actually running and timing problems on a computer. The latter approach has been used in the study, and for the two chemistry systems reported in Section 6, the rational approximation method requires significantly less computer time than standard methods. These timing studies have been performed without any particular attention given to optimizing the codes or logic.



## 2. STATEMENT OF THE WORK

Problems in chemical kinetics give rise to differential equations of the form:

$$\dot{y}_i = \sum_{j=1}^m (\nu''_{ij} - \nu'_{ij}) k_j(T) \rho^{-1} \prod_{\ell=1}^n (\rho y_{\ell})^{\nu'_{\ell j}} \quad i=1,2,\dots,n \quad (2.1)$$

where  $n$  is the number of reacting species,  $m$  is the total number of reactions (the sum of forward and reverse reactions),  $y_i$  is the number of moles per unit mass of the mixture, and the dot denotes differentiation with respect to time.  $T$  and  $\rho$  are the temperature and density, respectively. The stoichiometric coefficients  $\nu'_{ij}$  and  $\nu''_{ij}$  are defined by the following expression for the  $j^{\text{th}}$  chemical reaction equation:

$$\sum_{i=1}^n \nu'_{ij} R_i = \sum_{i=1}^n \nu''_{ij} P_i$$

where  $R_i$  and  $P_i$  are the reactants and products, respectively. The reaction rate for the  $j^{\text{th}}$  reaction is  $k_j$  which is taken as a function of temperature only and has the form

$$k_j(T) = a_j T^{b_j} \exp(-e_j/T)$$

where  $a_j$ ,  $b_j$ , and  $e_j$  are constants.

These equations define a system of  $n$  first order differential equations which can be expressed in general form as

$$\dot{y}(t) = f(t, y) ; \quad y(t_0) = y_0 \quad (2.2)$$

where  $y$  is a vector valued function of  $t$ ,  $(y_i(t))$  and  $f$  is a vector valued function of  $t$  and  $y$ ,  $(f_i(t, y_1, \dots, y_n))$ . Given the initial vector  $y_0$ , the system of ODE is to be integrated over the time domain  $(t_0, t_f)$ . To complete the specification of the problem, relationships are required for the computation of density and temperature. These relationships are the equation of state and a definition of enthalpy as a function of temperature.

Many methods have been devised for obtaining a numerical solution of (2.2). However, most of these methods will not give a valid solution if the stepsize  $h$  becomes too large. Although the truncation error increases in a smooth manner as  $h$  increases, the numerical solution becomes unstable when  $h$  exceeds a certain critical value. Even if the truncation or round-off errors are small, the propagated error becomes unbounded because the amplification term in the error expression has a spectral radius greater than one.

The unstable behavior can be illustrated and understood by considering the error behavior of the Euler method. Let

$$\bar{y}_{k+1} = \bar{y}_k + h\bar{f}_k \quad (2.3)$$

where  $\bar{f}_k = f(t_k, \bar{y}_k)$ ,  $h$  is the stepsize between  $t_{k+1}$  and  $t_k$ , and  $t_k = kh$ . The stepsize,  $h$ , can be assumed a constant for this discussion. The true solution can be expressed as

$$y_{k+1} = y_k + hf_k + \tau_{k+1} \quad (2.4)$$

where  $\tau_{k+1}$  is the truncation error. By subtracting (2.3) from (2.4), applying the mean value theorem, and letting  $e_k = y_k - \bar{y}_k$ , the error expression becomes

$$e_{k+1} = \left( I + h \frac{\partial f}{\partial y} \right) e_k + \tau_{k+1} \quad (2.5)$$

where  $\frac{\partial f}{\partial y}$  is the matrix  $\left[ \frac{\partial f_i}{\partial y_j} \right]$ . The operator on the error term  $e_k$  is the amplification matrix which determines the stability behavior of the system of equations. Dropping the truncation error and assuming that  $\frac{\partial f}{\partial y}$  is a constant (e.g. the vector  $f$  is a linear function of  $y$ ), an initial error vector  $e_0$  produces the following error vector after  $k+1$  steps:

$$e_{k+1} = \left( I + h \frac{\partial f}{\partial y} \right)^{k+1} e_0 \quad (2.6)$$

If the eigenvalues of  $\frac{\partial f}{\partial y}$  have positive real parts, the solution would be increasing and the error might also be expected to increase. However, if the eigenvalues all have negative real parts and an error increases from one step to the next, the numerical solution will then be partially unstable. A more complete discussion of stability will be found in Section 3, but the above description is adequate for our example.

If the error generated by Euler's method is not to increase, the eigenvalues of the amplification matrix  $I + h \frac{\partial f}{\partial y}$  must be less than one in absolute value. Otherwise, as the matrix is raised to higher powers, the norm of the error vector will continually grow. Let the  $l$ th complex eigenvalue of  $\frac{\partial f}{\partial y}$  be

$$\lambda_l = -\alpha_l + i\beta_l$$

where  $\alpha_l > 0$ . Then by imposing the stability requirement, a sufficient condition for stability is

$$h < 2/\hat{\alpha}$$

where  $\hat{\alpha} = \max_l |\operatorname{Re} \lambda_l|$

If  $\hat{\alpha}$  is large, as in the chemical kinetic case, this requirement may result in a small  $h$  and a large amount of computing time if the domain of integration is large. The above behavior for the Euler method is characteristic of most standard single and multi-step methods. Extending the analysis to the more complicated methods does not present any difficulty other than cumbersome algebra and has been reported in Ref. 3. For the purpose of later discussion, the stability criteria for the fourth order Runge Kutta method is

$$h < 2.8/|\lambda|$$

where  $\lambda$  is a real eigenvalue of the system.

In attempting to find a method for which the stepsize is not so dependent upon the magnitude of the eigenvalues of the system of equations being solved, an iterative method might be considered.

If the solution is iterated a number of times for each step, the error might not continually grow even though the stepsize is large.

Unfortunately, if the eigenvalues of the system are large, a small stepsize is necessary if the iterative method is to converge.

This can be illustrated by the following method based on the trapezoidal rule for integration

$$y_{k+1}^{i+1} = y_k + \frac{h}{2}(f_k + f_{k+1}^i)$$

where  $i$  is the index counter for the iterations. The difference  $d^{i+1}$  between the result at iteration  $(i+1)$  and  $(i)$  is (the index  $k$  is dropped for simplicity)

$$d^{i+1} = \frac{h}{2} \frac{\partial f}{\partial y} d^i = \frac{h}{2} \left( \frac{\partial f}{\partial y} \right)^{i+1} d^0$$

Again the matrix  $\frac{\partial f}{\partial y}$  was assumed constant. The matrix  $h \frac{\partial f}{\partial y}$  must be convergent; that is, its eigenvalues  $\lambda_\ell$  must have a modulus less than one. Hence, the stepsize must satisfy

$$h < 2/\hat{\lambda}$$

where  $\hat{\lambda} = \max_{\ell} |\lambda_\ell|$ .

Again if  $\hat{\lambda}$  is large, the stepsize is restricted to a very small value.

The equations describing the chemical reaction for the combustion of hydrogen in air can be used to illustrate the restriction on stepsize. In a typical case the solution might be desired over a time domain of .01 seconds. However, the magnitude of the largest eigenvalue of the system will be about  $10^6$ , and the Euler method would require a stepsize  $h < 2 \times 10^{-6}$  (seconds) to remain stable. Hence 5000 steps would be needed to complete the problem. Similarly the iteration method would require a great number of steps. These small steps are required even though little change might occur in the solution from one step to the next.

Other methods which are not stepsize limited because of stability must be considered. In the next section, several such methods will be discussed.

### 3. DEVELOPMENT OF STABLE INTEGRATION METHOD

In order to study the stability of a numerical method of solution for the system of ordinary differential equations (2.2), the nature of the solution must be discussed. If a component of the analytical solution is growing, the numerical error could also be expected to grow. This type of error growth which is due to the nature of the equations is not regarded as an instability of the numerical method. However, if an error, once introduced, continues to grow even though the transient part of the solution decays, the numerical method will not be stable. A decaying solution can be characterized by the fact that the eigenvalues of the matrix  $\partial f / \partial y$  whose general element is  $\partial f_i / \partial y_j$  will have negative real parts. These considerations lead to the following definition of numerical stability used in this report.

A numerical method of solution for ODE of the form (2.2) is stable if an error, once introduced, decreases from step to step when the eigenvalues of  $\partial f / \partial y$  have negative real parts.

As was shown in Section 2, many methods become unstable if the stepsize is too large. Methods will be developed in this section which are stable for any stepsize. The only restriction on the stepsize will be due to the error introduced by the nature of numerical approximations. This error, which is inherent in any

numerical method involving truncation and round-off, may accumulate but not grow in an unbounded manner. While these methods are developed for linear differential equations, it will be shown that they can also be applied to a general system of nonlinear equations which include the equations of chemical kinetics as a special case.

The method of derivation might best be understood by first considering a single ODE of the form

$$\dot{y} = ay + b.$$

Assume as a "trial family" solution a simple linear function of  $t$ ; that is,

$$y = y_0 + ct.$$

Now impose that the linear solution satisfies the differential equation at  $t=h$ . Hence,

$$c - a(y_0 + ch) - b = 0.$$

It then follows that

$$c = (ay_0 + b)/(1-ah) .$$

The solution would then be

$$y(h) = y_0 + (1-ah)^{-1} (ay_0 + b)h .$$



Alternatively, it could be required that

$$\int_0^h (\dot{y} - ay - b) dt = \int_0^h (c - ay_0 - act - b) dt = 0.$$

In this case the integral of the error in the approximation is made zero over the interval  $(0, h)$  and

$$c = (ay_0 + b) / (1 - \frac{1}{2} ah)$$

and

$$y(h) = y_0 + (1 - \frac{1}{2} ah)^{-1} (ay_0 + b)h.$$

These ideas will now be generalized to a system of equations and a polynomial of any order in  $t$ . Consider a system of  $N$  linear ODE with constant coefficients

$$\dot{y}(t) = Ay(t) + b \quad (3.1)$$

with initial conditions

$$y(t_0) = y_0$$

In order to solve these equations, assume a solution of the form

$$\bar{y}(t) = y_0 + \sum_{i=1}^m c_i t^i \quad (3.2)$$

where the  $c_i$  are to be determined in such a manner that  $\bar{y}(t)$  satisfies equation (3.1) in the interval  $(0, h)$  with the error  $e(t)$ .

Substituting (3.2) into (3.1) leads to the equation

$$e(t) = \sum_{i=1}^m i c_i t^{i-1} - A y_0 - \sum_{i=1}^m A c_i t^i - b \quad (3.3)$$

The coefficients  $c_i$  can be determined by weighing the error  $e(t)$  by several different methods. The method of collocation would require that the error vanish at specified points in the interval whereas a subdomain technique requires the integrated error to be zero over various subintervals. Expressed in equation form, these two methods impose

$$\text{collocation: } e(t_j) = e\left(\frac{jh}{m}\right) = 0 \quad \text{for } j=1,2,\dots,m \quad (3.4)$$

$$\text{subdomain: } \int_{t_{j-1}}^{t_j} e(t) dt = 0 \quad \text{for } j=1,2,\dots,m \quad (3.5)$$

Although other techniques such as Galerkin or least squares, which impose still different conditions on the error, are useful in various types of problems, these methods do not seem to offer any advantage toward the development of stable integration procedures. As will be shown subsequently, the class of stable methods can be represented in a general form and consideration of the Galerkin or least squares method is not necessary nor desirable from the viewpoint of truncation error.

For the collocation method, the following equations for the  $c_i$  are obtained from (3.4) and (3.3):

$$\sum_{i=1}^m \left(\frac{jh}{m}\right)^{i-1} \left(iI - \frac{jh}{m} A\right) c_i = A y_0 + b \quad j=1,2,\dots,m \quad (3.6)$$

Similarly for the subdomain method using (3.5) and (3.3), we obtain

$$\sum_{i=1}^m \left( \frac{jh}{m} \right)^{i-1} \left( I - \frac{1}{i+1} \frac{jh}{m} A \right) c_i = Ay_0 + b \quad j = 1, 2 \dots m \quad (3.7)$$

Using either (3.6) or (3.7), a set of coefficients  $c_i$  can be computed and upon introducing these coefficients into equation (3.2), the desired integration formulas can be obtained. The details of the algebraic operations appear in Appendix A for  $m = 1$  and 2, and only the final integration formulas are tabulated below:

#### Collocation Method

$$y(h) = y_0 + h(I-hA)^{-1} (Ay_0 + b) \quad (3.8)$$

$$= (I-hA)^{-1} (y_0 + hb)$$

for  $m = 1$

$$\begin{aligned} y(h) &= y_0 + h \left( I - 3/4 hA + 1/4 h^2 A^2 \right)^{-1} (I - 1/4 hA) (Ay_0 + b) \\ &= \left( I - 3/4 hA + 1/4 h^2 A^2 \right)^{-1} \left[ (I + 1/4 hA)y_0 + (I - 1/4 hA)hb \right] \end{aligned} \quad (3.9)$$

for  $m = 2$

#### Subdomain Method

$$y(h) = y_0 + h(I - 1/2 hA)^{-1} (Ay_0 + b) \quad (3.10)$$

$$= (I - 1/2 hA)^{-1} \left[ (I + 1/2 hA)y_0 + hb \right]$$

for  $m = 1$

$$\begin{aligned}
y(h) &= y_0 + h \left[ I - \frac{1}{2} hA + \frac{1}{12} (hA)^2 \right]^{-1} (Ay_0 + b) \\
&= \left[ I - \frac{1}{2} hA + \frac{1}{12} (hA)^2 \right]^{-1} \left[ \left( I + \frac{1}{2} hA + \frac{1}{12} (hA)^2 \right) y_0 + hb \right] \\
&\qquad\qquad\qquad \text{for } m = 2 \qquad (3.11)
\end{aligned}$$

High order integration procedures ( $m > 2$ ) can be obtained in a similar manner. However, from the viewpoint of application to the problems of chemical kinetics, these higher order schemes are not of great interest. As will be illustrated in Section 4, the residual error introduced by linearizing the ODE negates any advantage derived from the small truncation error achieved with higher order methods.

Having once derived formulas (3.8) through (3.11), several other interpretations may be given. For example, the formulas can be developed for integrating  $y'$  between the points  $t = t_0$  and  $t = t_0 + h$  in the following manner. If the lowest order implicit integration formula is applied to the system of equations (3.1)

$$y(h) = y_0 + h \dot{y}(h) = y_0 + h (Ay(h) + b)$$

and upon transposing

$$(I - hA) y(h) = y_0 + hb$$

or

$$y(h) = (I - hA)^{-1} (y_0 + hb)$$

The above equation is the previously derived equation (3.8).

When  $\dot{y}$  is integrated using the trapezoidal rule

$$y(h) = y_0 + 1/2 h (\dot{y}_0 + \dot{y}(h)) = y_0 + 1/2 h (A y_0 + b + A y(h) + b)$$

Transposing and solving

$$y(h) = (I - 1/2 h A)^{-1} [(I + 1/2 h A) y_0 + h b]$$

The above equation corresponds to equation (3.10) for the sub-domain method with  $m=1$ .

The second order equation (3.9) for collocation is obtained when more weight is given to the right end point. By introducing the second derivative into the integration formula

$$\begin{aligned} y(h) &= y_0 + 1/4 h (\dot{y}_0 + 3\dot{y}(h)) - 1/8 h^2 \ddot{y}(h) \\ &= y_0 + 1/4 h (A y_0 + b + 3A y(h) + 3b) - 1/8 h^2 A (A y(h) + b) \end{aligned}$$

Then rearranging

$$y(h) = (I - 3/4 h A + 1/4 (h A)^2)^{-1} ((I + 1/4 h A) y_0 + (I - 1/4 h A) h b)$$

Finally a formula can be obtained which utilizes the interpolating polynomial in terms of  $\dot{y}$  and  $\ddot{y}$  at both end points of the step, and

$$y(h) = y_0 + 1/2 h(\dot{y}_0 + \dot{y}(h)) - 1/12 h^2 (\ddot{y}(h) - \ddot{y}_0)$$

$$= y_0 + 1/2 h(Ay_0 + b + Ay(h) + b) - 1/12 h^2 A(Ay(h) + b - Ay_0 - b)$$

Rearranging the terms,

$$y(h) = (I - 1/2 hA + 1/12(hA)^2)^{-1} [(I + 1/2 hA + 1/12(hA)^2)y_0 + hb]$$

Thus the integration procedure (3.11) derived from the subdomain method with  $m=2$  is obtained.

Hence all of the integration procedures obtained from the polynomial trial family approach have interpretations in terms of other integration formulas after suitable algebraic manipulation. This manipulation of the integration formulas is possible because the system of equations is linear and suggests the possibility of a general approach to the derivation of integrators using known properties of linear ODE. The formal solution of equation (3.1) at  $t=h$  is

$$y(h) = y_0 + [\exp(hA) - I] A^{-1} (Ay_0 + b) \quad (3.12)$$

where

$$\exp(hA) = I + hA + 1/2 (hA)^2 + \dots$$

Equation (3.12) is similar in form to the numerical integration formulas (3.8) through (3.11). The equations become identical if the exponential term in (3.12) is replaced by the corresponding rational approximations in the integration formulas.

Further study indicates that with the exception of (3.9), the rational approximations are identical with those obtained from the Pade' table for the exponential function. Each of the entries in the table are polynomials P and Q of degree p and q, respectively, such that

$$e^{hA} = Q^{-1} P + E(hA)$$

that is, the rational approximation agrees with the power series of  $\exp(hA)$  for at least  $p + q + 1$  terms. The residual error is denoted by  $E(hA)$ . The polynomials in the Pade' Table for the exponential function (Ref.4) are given by

$$P = \sum_{k=0}^p \frac{(p+q-k)! p!}{(p+q)! k! (p-k)!} (hA)^k$$

$$Q = \sum_{k=0}^q \frac{(p+q-k)! q!}{(p+q)! k! (q-k)!} (-hA)^k$$

By evaluating these formulas for the following three cases:

(1)  $p=0, q=1$ , (2)  $p=q=1$ , and (3)  $p=q=2$ , and applying the results to equation (3.12), the integration equations (3.8), (3.10) and (3.11) are obtained, respectively. Equation (3.9) cannot be derived from the Pade' table, but in the next section it will be shown that the corresponding Pade' table entry for  $p=1$  and  $q=2$  is similar and has a smaller truncation than (3.9).

By using the Pade' table, the different integration formulas can be derived in a unified manner, and very little effort is needed to develop formulas of any order. The truncation error of these formulas may also be obtained directly from the Pade' theory. Because of the general nature of such Pade' approximation, integration formulas which arise from them shall be called Pade' integration formulas.

These methods must now be examined from the viewpoint of stability. All of the methods discussed are of the form

$$\bar{y}(h) = Q^{-1} P y_0 + Q^{-1} Rb$$

where  $R$  represents some polynomial in  $(hA)$ . Applying the method in a step by step manner yields

$$\bar{y}_{k+1} = Q^{-1} P \bar{y}_k + Q^{-1} Rb \quad (3.13)$$

where  $y_k = y(kh)$ . The true solution  $y$  can also be expressed as

$$y_{k+1} = Q^{-1} P y_k + Q^{-1} Rb + \tau_{k+1} \quad (3.14)$$

where  $\tau_{k+1}$  is the truncation error. Denote the error at each step by

$$e_k = y_k - \bar{y}_k$$

and subtract (3.13) from (3.14) to obtain



$$e_{k+1} = (Q^{-1}P) e_k + \tau_{k+1} . \quad (3.15)$$

In order to see how an error from any source propagates, we may neglect the truncation error term and assume that a single error  $e_0$  is committed at one step, say the first step. Equation (3.15) then becomes

$$e_k = Q^{-1} P e_{k-1} = (Q^{-1}P)^2 e_{k-2} = \dots = (Q^{-1}P)^k e_0 \quad (3.16)$$

After  $k$  steps an initial error  $e_0$  will grow or decay depending upon the amplification matrix  $(Q^{-1}P)$ .

From the definition of stability, when the eigenvalues of the matrix  $A$  have negative real parts,  $e_k$  must decrease as  $k$  increases. Since  $e_0$  is a constant,  $e_k$  can decrease only if the matrix  $(Q^{-1}P)^k$  is convergent; that is, the eigenvalues of  $(Q^{-1}P)$  must be less than one in absolute value. For every eigenvalue  $\lambda_i$  of the matrix  $A$  in (3.1), there is a corresponding eigenvalue for  $Q^{-1}P$ . For convenience, the stability criteria is stated in terms of  $\lambda$  by using

$$\left| P(\bar{\lambda})/Q(\bar{\lambda}) \right| < 1$$

Thus the stability requirement becomes

$$|P(\bar{\lambda})| < |Q(\bar{\lambda})| \quad (3.17)$$

where the complex eigenvalue  $\bar{\lambda} = h\lambda = -\alpha + i\beta$  ( $\alpha > 0$ ). In the following table, the complex eigenvalue polynomials for  $P(\lambda)$  and  $Q(\lambda)$  are given for each integration procedure.

Table of Complex Eigenvalue Polynomials

Equation No.	$P(\bar{\lambda})$	$Q(\bar{\lambda})$
3.8	1	$(1+\alpha) - i\beta$
3.9	$(1 - \frac{1}{4}\alpha) + \frac{1}{4}i\beta$	$1 + \frac{3}{4}\alpha + \frac{1}{4}(\alpha^2 - \beta^2) - i\beta(\frac{3}{4} + \frac{1}{2}\alpha)$
3.10	$(1 - \frac{1}{2}\alpha) + \frac{1}{2}i\beta$	$(1 + \frac{1}{2}\alpha) - \frac{1}{2}i\beta$
3.11	$1 - \frac{1}{2}\alpha + \frac{1}{12}(\alpha^2 - \beta^2) + i\beta(\frac{1}{2} - \frac{1}{6}\alpha)$	$1 + \frac{1}{2}\alpha + \frac{1}{12}(\alpha^2 - \beta^2) - i\beta(\frac{1}{2} + \frac{1}{6}\alpha)$

The tabulated values of  $P(\bar{\lambda})$  and  $Q(\bar{\lambda})$  satisfy the stability criteria (3.17), and, consequently, all of the integration procedures are stable within our definition. Since the stepsize,  $h$ , does not explicitly enter into the above analysis, our conclusions are for all values of  $h$ .

#### 4. ERROR BEHAVIOR OF THE RATIONAL APPROXIMATION METHODS

Once a numerical method for solving a problem has been developed, it must be examined to establish how well it approximates the actual solution to the problem. If the error cannot be kept within reasonable bounds, the method will not be of any practical value. For a known initial error, the investigation of stability (Section 3) indicates the behavior of the error growth or decay as the integration continues from step to step. In this section, the methods of integration will be examined from the viewpoint of the types of errors introduced at each step by the numerical approximations. These errors are caused by the truncation in our integration formulas, the residual error introduced by linearizing the equations at each step and round-off. The former two sources of error will be discussed, but the latter type of error will not be considered in this report.

The step by step truncation error of any of the formulas (3.8) through (3.11) may be evaluated with the help of Taylor's formula. The solution of (3.1) may be written as

$$\begin{aligned} y(h) &= y_0 + h\dot{y}(0) + \frac{1}{2!} h^2 \ddot{y}(0) + \dots + \frac{1}{(n+1)!} h^{n+1} y^{(n+1)}(\eta) \\ &= y_0 + h\dot{y}(0) + \frac{1}{2!} h^2 A\ddot{y}(0) + \dots + \frac{1}{(n+1)!} h^{n+1} A^n \dot{y}(\eta) \end{aligned}$$

$$(0 \leq \eta \leq h) \quad (4.1)$$

since (3.1) may be differentiated to yield  $y^{(n)}(t) = A^{n-1} \dot{y}(t)$ .

Each of the integration formulas (3.8) through (3.11) can be expanded and compared with (4.1) to obtain the truncation error  $\tau$ . For example, equation (3.8) can be expanded as

$$\bar{y}(h) = y_0 + h\dot{y}_0 + (I-hA)^{-1} h^2 A\dot{y}_0 \quad (4.2)$$

Subtracting (4.2) from (4.1) defines the truncation error

$$\tau = h^2 A(I-hA)^{-1} \left[ \frac{1}{2} (I-hA)\dot{y}'(\eta) - \dot{y}'(0) \right] \quad (4.3)$$

If  $(hA)$  is a convergent matrix, then

$$\tau = - \frac{h^2 A}{2} \dot{y}'(\xi) = O(h^2 A) \quad (4.4)$$

Similar expressions for truncation error can be derived for all of the rational approximations and are tabulated below:

TABLE I - TRUNCATION ERRORS

<u>Formula No.</u>		<u>Behavior</u>
(3.8)	$h^2 A \left[ \frac{1}{2} \dot{y}'(\eta) - (I-hA)^{-1} \dot{y}_0 \right]$	$O(h^2 A)$
(3.9)	$h^3 A^2 \left[ \frac{1}{6} \dot{y}'(\eta) - \frac{1}{8} (I - \frac{3}{4} hA + \frac{1}{4} h^2 A^2)^{-1} (I-hA)\dot{y}_0 \right]$	$O(h^3 A^2)$

TABLE I - TRUNCATION ERRORS (CONT)

<u>Formula No.</u>		<u>Behavior</u>
(3.10)	$h^3 A^2 \left[ \frac{1}{6} \dot{y}(\eta) - \frac{1}{4} \left( I - \frac{1}{2} hA \right)^{-1} \dot{y}_0 \right]$	$O(h^3 A^2)$
(3.11)	$h^5 A^4 \left[ \frac{1}{120} \dot{y}(\eta) - \frac{1}{144} \left( I - \frac{1}{2} hA + \frac{1}{12} h^2 A^2 \right)^{-1} \right. \\ \left. \left( I - \frac{1}{2} hA \right) \dot{y}_0 \right]$	$O(h^5 A^4)$

The truncation error can also be derived using the theory of Padé' approximations. The Padé' rational approximations, which have a numerator and a denominator that are polynomials of degree  $p$  and  $q$ , respectively, agree with the Taylor's series expansion of the function for at least  $p + q + 1$  terms. In this sense, it is the "best" approximation. As mentioned in Section 3, formula (3.10) corresponds to  $p = q = 1$ , and then from the remainder term in Taylor's formula the truncation term must be  $O(h^3)$  which is the value given in the above table. Similar results can be established for formulas (3.8) and (3.11) for the cases of  $p = 0, q = 1$ , and  $p = q = 2$ , respectively. Now consider the equivalent Padé' approximation for (3.9) which requires  $p = 1$  and  $q = 2$ . For these values, the approximation to the exponential is

$$e^{hA} \doteq Q^{-1} P = \left[ I - \frac{2}{3} hA + \frac{1}{6} (hA)^2 \right]^{-1} \left[ I + \frac{1}{3} hA \right]$$

and the corresponding truncation error is  $O(h^4)$ . However, from the table for (3.9),  $\tau = O(h^3)$  indicating a less accurate integration formula.

The truncation error in Table I can be used in the usual manner; namely, the behavior of the error for various stepsizes can be predicted and for sufficiently small values of  $h$  the accuracy of various methods compared. For example, the error for (3.11) is comparable to the fourth order Runge-Kutta method.

Now consider the nonlinear system of ODE (2.2), which are rewritten here

$$\dot{y} = f(t, y) ; \quad y(t_0) = y_0 . \quad (2.2)$$

The system is reduced to the form of (3.1) by expanding the function  $f$  in a Taylor's Series and neglecting high order terms:

$$\dot{y} = f(t_0, y_0) + \frac{\partial f}{\partial y}(t_0, y_0) \Delta y + O(\Delta y^2) \quad (4.5)$$

where  $\Delta y = y - y_0$  and  $\frac{\partial f}{\partial y}(t_0, y_0)$  denotes the matrix  $A$  in (3.1) with elements

$$a_{ij} = \frac{\partial f_i}{\partial y_j} .$$

The indices  $i$  and  $j$  denote the  $i^{\text{th}}$  and  $j^{\text{th}}$  elements in the  $f$  and  $y$  vectors, respectively. Hence grouping terms as in (3.1)

$$\begin{aligned} \dot{y} &= \frac{\partial f}{\partial y}(t_0, y_0)y + (f(t_0, y_0) - \frac{\partial f}{\partial y}(t_0, y_0)y_0) + O(\Delta y^2) \\ &= Ay + b + O(\Delta y^2) \end{aligned}$$

Since the equation must be linearized at each step of the integration, the residual error, which is denoted by  $\epsilon_{k+1} = O(\Delta y^2)$

for the  $k^{\text{th}}$  step, must be introduced in equation (3.15),

$$e_{k+1} = (Q^{-1}P)e_k + Q^{-1}R \ell_{k+1} + \tau_{k+1} \quad (4.6)$$

Again, assuming the matrix  $A$  and the vector  $b$  are nearly constant over  $(k+1)$  steps then

$$e_{k+1} = (Q^{-1}P)^{k+1} \left[ e_0 + \sum_{\nu=1}^{k+1} (Q^{-1}P)^{-\nu} (Q^{-1}R \ell_{\nu} + \tau_{\nu}) \right] \quad (4.7)$$

Equation (4.7) which is similar to (3.16) includes the influence of the truncation error and the residual error of linearization. Again, the amplification matrix  $Q^{-1}P$  must be a convergent matrix for a stable system. The rate of decay of  $(Q^{-1}P)^k$  and the magnitude of the error  $Q^{-1}R \ell_k + \tau_k$  introduced at each step will determine whether  $e_{k+1}$  is decreasing with  $k$ . Since the linearization and the truncation errors appear together, the integration method for a particular type of problem should be selected to achieve a truncation error approximately the same size as the linearization error. Hence, if a large residual error is present, a low order integration formula should be used.

## 5. IMPLEMENTATION ON A DIGITAL COMPUTER

The Pade' approximations for integration have been used to solve two sets of differential equations of the form (2.1) arising from two different chemistry systems. The reaction equations and resulting differential equations for these systems will be found in Appendix B. Although the equations of the systems are similar in form their solutions have different characteristics. Chemistry systems which are significantly different in behavior have been chosen to demonstrate the suitability of the integration procedures under consideration. One system represents hydrogen burning in air. Initially, the species that were zero become larger while the temperature remains almost constant. Then ignition occurs and the temperature and species change rapidly over a short interval. Finally the process slows down as equilibrium is approached. The second chemistry system is for dissociating air with the charged species restricted to  $\text{NO}^+$  and  $\text{e}^-$ . The initial conditions are taken directly behind a bow shock, assuming the species are frozen across the shock. The species that were initially zero almost immediately assume large values, while the temperature rapidly decreases. The digital computer programs for these two chemistry systems use similar integration procedures but vary in programming details as will be described below.



In order to use the Pade' integration method, eq. (2.1) must be linearized. This equation can be written in the general form  $\dot{y} = f(y, T, \rho)$ , and when expanded through first order terms, the linearized equation becomes

$$\dot{y} = f(y_0, T_0, \rho_0) + (\partial f / \partial y)_0 \Delta y + (\partial f / \partial T)_0 \Delta T + (\partial f / \partial \rho)_0 \Delta \rho \quad (5.1)$$

where  $y$ ,  $f$ ,  $\partial f / \partial T$  and  $\partial f / \partial \rho$  are vectors,  $\partial f / \partial y$  is a matrix and  $( )_0$  implies the function is evaluated at the beginning of the step. The form of  $\partial f / \partial y$  for the two chemistry systems under consideration will be found in Appendix B.

To clearly understand the results of the linearization, a typical term will be examined. Such a term might have the form

$$R_j = k_j(T) \rho y_r y_s$$

Now expanding  $R_j$  through second order terms,

$$\begin{aligned} R_j \approx & (k_j(T) \rho y_r y_s)_0 + (k_j(T) \rho y_s)_0 \Delta y_r + (k_j(T) \rho y_r)_0 \Delta y_s \\ & + \left( \frac{\partial k}{\partial T}(T) \rho y_r y_s \right)_0 \Delta T + (k_j(T) y_r y_s)_0 \Delta \rho + (2k_j(T) \rho)_0 \Delta y_r \Delta y_s \\ & + \left( 2 \frac{\partial k}{\partial T}(T) \rho y_s \right)_0 \Delta T \Delta y_r + \left( 2 \frac{\partial k}{\partial T}(T) \rho y_r \right)_0 \Delta T \Delta y_s + (2k_j(T) y_s)_0 \Delta \rho \Delta y_r \\ & + (2k_j(T) y_r)_0 \Delta \rho \Delta y_s + \left( 2 \frac{\partial k}{\partial T}(T) y_r y_s \right)_0 \Delta \rho \Delta T + \left( \frac{\partial^2 k}{\partial T^2}(T) \rho y_r y_s \right)_0 \Delta T^2 \end{aligned} \quad (5.2)$$

There are linear terms in  $\Delta T$  and  $\Delta \rho$  in addition to the linear term in  $\Delta y_1$ . Unfortunately, the temperature and density are not derived from differential equations and hence cannot appear explicitly in the integration scheme. The temperature is obtained by using polynomial fits of enthalpy tables and the equation of state is used for the density. In the hydrogen case, the enthalpy for each species is a linear function of temperature over the entire region of interest. For the air chemistry, the enthalpy is approximated by quadratic fits over three discrete temperature intervals which cover the region from 0 to 6000°K. The coefficients and other details of the fits are listed in Appendix B.

The significant changes in the temperature and density for the hydrogen-air reaction are confined to a small portion of the domain of integration  $(t_o, t_f)$ . With respect to an integration step, the change in these parameters is relatively small, and consequently, the linear terms involving  $\Delta \rho$  and  $\Delta T$  are neglected along with all higher order terms. Then the simplified linear approximation becomes:

$$R_j \approx (k_j(T) \rho y_r y_s)_o + (k_j(T) \rho y_s)_o \Delta y_r + (k_j(T) \rho y_r)_o \Delta y_s \quad (5.3)$$

These simplifications are not possible for the air chemistry system, because of the large change in temperature (e.g. 1000°K) which can occur over an integration step. The production terms

for air are similar to (5.3) but with the term  $(k_j(T)\rho y_r y_o)_o \Delta T$  which is added to the constant term in the digital computer program. Initially,  $\Delta T$  is unknown and the program has been designed to iterate until the solution converges on the correct value. The density term involving  $\Delta \rho$  has been dropped in the linearized form for the air chemistry since its numerical magnitude was negligible compared to other terms. However, with additional effort, the term could be included by considering the density a function of temperature as expressed by the equation of state and combining with the other terms in the linearized equation.

For the hydrogen-air chemistry system, the integration method (3.11) has been used in the digital computer program. For simplicity in the logic of the program, the stepsize is held constant over the domain of integration. A brief summary of the operations and their order of execution in the program are given below:

1. The inputs for a problem are read-in and the program is initialized.
2. The temperature is computed using the definition of enthalpy, i.e.  $h = \sum \alpha_i h_i(T)$  where  $\alpha_i$  are the mass fractions and  $h_i$  are the enthalpy fits of the species on page 46..
3. The density is computed from the equation of state

$$\rho = \frac{P}{RT \sum y_i}$$

4. The linearized form of the differential equations is computed i.e., the A matrix and b vector of equation (3.1) are formed. The equations for the elements  $a_{ij}$  of A appear on page 49..
5. Using (3.11) as an integration procedure, the species at step (k+1) are computed.
6. Time is incremented by the stepsize h.
7. Steps 2 through 6 are repeated until the entire domain  $(t_o, t_f)$  is covered.

In the air chemistry system the residual error due to linearization is larger than in the hydrogen air system. Consequently, a low order integration procedure is adequate from the viewpoint of consistency between the residual and truncation errors. For this reason, the digital computer program has been designed around integration procedure (3.10). For simplicity the original program assumed a constant stepsize. However, the behavior of the solution immediately indicated that a variable stepsize would be very advantageous, and the logic for a variable stepsize has been introduced. (In Section 6, results from both programs are given). The sequence of steps in this digital computer program is as follows:

1. The inputs for a problem are read-in and the program is initialized.
2. The temperature is computed from the definition of enthalpy using a Newton Raphson iteration procedure. The enthalpy fits appear on page 52 .

3. The change in temperature  $\Delta T$  is calculated for use with the linearized equations.
4. If after the first integration step, the temperature change does not agree with the predicted  $\Delta T$ , a regula-falsi iteration method is started and steps 3 through 8 are repeated until the sequence  $\Delta T^{(1)}, \Delta T^{(2)}, \dots$  converges.
5. If  $\Delta T$  is larger than a maximum input value  $\Delta T_{\max}$ , the stepsize  $h$  is halved and the integration repeated with the new stepsize. If  $2\Delta T < \Delta T_{\max}$ , the stepsize  $h$  is doubled.
6. The density is computed from the equation of state.
7. The linearized form of the differential equation is computed; the contribution from the  $\Delta T$  temperature term is included in the  $b$  vector of equation (3.1). The  $A$  matrix is defined by the equations on page 55.
8. Using (3.10) as an integration procedure, the species at step  $(k+1)$  are computed.
9. Time is incremented by the current stepsize.
10. Steps 2 through 9 are repeated until the domain  $(t_o, t_f)$  is covered.

Regarding the method of programming any of the integration procedures (3.8) through (3.11), the inversion of a matrix is not required. Rather the solution for  $y_{k+1}$  is obtained by solving a system of linear simultaneous equations. The coefficient matrix is shown inverted in equation (3.8) through (3.11).

## 6. DISCUSSIONS OF NUMERICAL RESULTS

The two chemistry models which have been studied are conveniently compared by the temperature curves shown in Figure 1. The lower temperature curve is for a hydrogen combustion reaction. In the initial region, temperature is almost constant, but as will be subsequently shown in Figures 3 through 5 some of the species are rapidly changing. At about  $.5 \times 10^{-3}$  seconds, the temperature begins increasing in the ignition region. In the final region which is not included on the graph, the temperature changes slowly with time as the mixture approaches equilibrium. The reaction was studied over a time domain of approximately .1 second and during this period the temperature changed about  $1000^{\circ}\text{K}$ .

The upper curve in Figure 1 is for the air chemistry system described in Appendix B. The problems investigated are typical of the phenomenon directly behind the bow shock of a re-entry vehicle. The free stream concentrations of species, which are assumed frozen across the shock, are the initial conditions for the chemical reaction system. The temperature immediately begins a rapid change from its initial value at  $23,000^{\circ}\text{K}$ , and in about  $5 \times 10^{-5}$  seconds, the temperature is reduced to  $8000^{\circ}\text{K}$ . During the remaining portion of the reaction, the temperature changes slowly as the mixture approaches equilibrium at about  $7400^{\circ}\text{K}$ .

From the numerical analysis results in Section 4, an interesting observation can be made about the numerical behavior of these two chemistry systems. Because the hydrogen system undergoes relatively small temperature changes with time, the residual error

from linearization will not be as large as in the case of the air chemistry. Hence, the stepsize for the hydrogen system should be substantially larger than the stepsize of the air system. In fact, the hydrogen system required a stepsize which was  $5 \times 10^{-5}$  and the largest stepsize for the air system was only  $5 \times 10^{-7}$ .

In Figure 2, the solid curve represents temperature as a function of time computed from the Runge-Kutta scheme for hydrogen chemistry with the following initial conditions:

$$T = 1100^{\circ}\text{K}$$

$$P = .135 \text{ atm (constant throughout the run)}$$

$$\alpha_{\text{H}} = .1277 \times 10^8 \qquad \alpha_{\text{O}} = .2106 \times 10^{-8}$$

$$\alpha_{\text{H}_2\text{O}} = 0.0 \qquad \alpha_{\text{OH}} = 0.0$$

$$\alpha_{\text{O}_2} = .2291069 \qquad \alpha_{\text{H}_2} = .014319$$

$$\alpha_{\text{N}_2} = .756574 \qquad (\text{a constant})$$

where  $\alpha$  is the mass fraction. The stable stepsize,  $h_s$ , according to Section 2 is approximately  $2.5 \times 10^{-6}$  seconds. For the purpose of the actual calculation, a stepsize of  $2 \times 10^{-6}$  has been used over the entire domain of integration. The same calculation has been repeated using the rational approximation method (3.11) for several different stepsizes. Some of the temperature results are shown for  $h = 25 h_s$  and  $50 h_s$  in Figure 2. The large stepsize produces a maximum error of approximately 4 per cent which is

a satisfactory agreement for this type of problem. For  $h = 50 h_s$ , the entire error curve of temperature is also shown in Figure 2. The error is a maximum in the region where the temperature derivative is large, as would be expected from the error propagation expression.

The species calculations for the same problem are found in Figure 3, 4 and 5 for  $\alpha_H$ ,  $\alpha_{H_2}$  and  $\alpha_{OH}$ , respectively. From these figures, it is evident that the rational approximation method produced good agreement with the Runge-Kutta method for  $h = 25 h_s$ . If  $h = 50 h_s$ , somewhat larger errors are produced, but depending upon the application even these results are satisfactory if some of the detail in the ignition region is not required. Regarding the use of very large stepsizes, the reason for the restriction  $h \leq 50 h_s$  is evident in Figure 4. If a stepsize of  $100 h_s$  is used, only two points would be available to define the step function behavior in the species  $\alpha_{H_2}$ . The truncation error upon leaving this region would be very large ( $|\dot{y}|$  is large) and this error would propagate throughout the solution. Furthermore, because the errors are reduced by  $(Q^{-1}P)$ , fewer steps implies the rate of decay would be reduced. These trends are even evident for the run where  $h = 50 h_s$ . At  $t = 6 \times 10^{-4}$  the result is much lower than the actual solution. Yet the numerical method successfully corrects this error at the next step indicating a stable behavior.

The comparison of the machine time required to integrate the equations over the interval  $(0, .05)$  is indicated in the following table:



TABLE II - COMPARISON OF MACHINE TIME

<u>Method</u>	<u>Number of Steps</u>	<u>(Running Time of Method)</u> <u>(Time of Runge-Kutta Method)</u>
Runge-Kutta	2500	1
(3.11) with $h = 25 h_s$	100	.08
(3.11) with $h = 50 h_s$	50	.04

Based upon only stepsize considerations, the rational method (3.10) should be 25 to 50 times as fast as the Runge-Kutta procedure. As mentioned before, the rational method requires the solution of a set of linear simultaneous equations at each integration step, and because of these added operations, the saving in over-all running time is not directly proportional to the decrease in the number of steps. However, as indicated in Table II, the rational approximation method can reduce the required machine time by a factor of 10 to 20. This reduction can be achieved without any effort to optimize the code or the application of ingenious methods to perform some of the operations.

In Figures 6 and 7 some of the results from the study of air chemistry are shown. For this particular problem the following initial conditions behind a bow shock have been used:

$$T_o = 23000^{\circ}\text{K} \quad p = 2.82 \text{ atmospheres (constant)}$$

$$\alpha_{O_2} = .238, \quad \alpha_{N_2} = .762, \text{ all other mass fractions are zero.}$$

The solid curves again are results from the Runge-Kutta procedure with a constant stepsize that is smaller than the stability limit. The maximum stable stepsize,  $h_s$ , is  $1 \times 10^{-8}$  as indicated by the dominant negative eigenvalues (see Table III) which incidently are almost constant over the major portion of the time interval. The dashed curves are results from the rational approximation method (3.10) with  $h = 20 h_s$ . The calculation was started at  $t = 2 \times 10^{-7}$  seconds with the initial value of the species taken from the Runge-Kutta calculation. There are two reasons for not starting the calculation at  $t=0$ . First, the temperature is changing rapidly near the origin. Using a large stepsize, the temperature must change  $9000^\circ\text{K}$  in the first step, and the residual error due to linearization would be excessive. Even with the iteration procedure described in Section 5, a suitable correction for such a large error would not be possible. A second reason for starting the calculation away from the origin is indicated in Figure 7 for the mass fraction  $\alpha_{\text{NO}^+}$ . With a large stepsize, the initial detail of the solid curve would have been lost.

The same problem was rerun with the identical stepsize, and numerical procedure, but the starting point was at  $t = 4 \times 10^{-7}$  seconds. These results are denoted by the symbol  $\odot$  in Figures 6 and 7. There is close agreement with the results from the Runge-Kutta procedure. Using a stepsize of  $50 h_s$ , the problem was run a third time and the results are denoted by the symbol  $\square$ . As would be expected, the larger the stepsize, the more error in the results. The maximum error is about 13 per cent for  $\alpha_{\text{NO}^+}$  in Figure

TABLE III - DOMINANT NEGATIVE EIGENVALUE OF THE "A" MATRIX  
AS A FUNCTION OF TIME - AIR CHEMISTRY

<u>Time x 10<sup>7</sup> (sec)</u>	<u>Eigenvalue</u>
0	- 2.21 x 10 <sup>8</sup>
.2	- 2.69 x 10 <sup>8</sup>
.8	- 2.92 x 10 <sup>8</sup>
1.2	- 2.89 x 10 <sup>8</sup>
2.0	- 2.84 x 10 <sup>8</sup>
8.0	- 2.67 x 10 <sup>8</sup>
10.0	- 2.65 x 10 <sup>8</sup>
20.0	- 2.57 x 10 <sup>8</sup>

7 at  $t = .8 \times 10^{-6}$  seconds. This error is attributed to the large change in temperature and species over a single step.

From the above discussion, it should be evident that a variable stepsize would be advantageous for this class of air chemistry problems. Initially, a small step is desirable to adequately define the changes in the species, and a very large step is suitable later in the reaction. Consequently, a very simple control on the stepsize has been introduced into the program (see Section 5). The program halves or doubles the stepsize depending upon the percent change in the temperature. With such a program, two runs have been made and the results appear in Figures 8, 9 and 10. The agreement between the results from the Runge-Kutta procedure and the variable stepsize runs is exceptionally good. Run No. 2, which permitted the temperature to change two per cent before halving the stepsize, extended over the time interval  $(0.1 \times 10^{-5})$  and required 1/5 to 1/6 the time of the Runge-Kutta procedure. Even a more significant reduction in the machine time can be expected for more difficult air chemistry problems. For example, results from air chemistry systems in stream tube calculations indicate that the rational approximation method can reduce the machine time by a factor of 15 to 20.

The digital computer programs used to obtain the numerical results for the hydrogen chemistry system were written in FORTRAN language for use on the CDC 160A and the IBM 7094. The air chemistry results were obtained from digital computer programs written in FORTRAN IV for use on the IBM 7094.

## 7. CONCLUSIONS

Four of the rational approximation methods of integration have been studied for their stability and propagated error characteristics. These methods were shown to be stable for all step-sizes and therefore more suitable for the integration of chemical kinetic equations than standard methods which are partially unstable. The only limitation on the stepsize is caused by the truncation error and the residual error introduced by the linearization of the original equations. However, the limitation is not severe since the stepsize for the rational approximation is still significantly larger than for standard methods.

The methods of integration have been applied to two different chemistry systems. In the case of the hydrogen-air combustion problem, the results from the rational approximation method agree well with results from the Runge-Kutta procedure. The required machine time was reduced by a factor of 10 to 20. Also for an air chemistry system, accurate results have been obtained and only 1/5 to 1/6 of the machine time used by the Runge-Kutta procedure was required. Even much larger reductions in machine time (15 to 20) have been achieved without any significant loss of accuracy by relaxing the criteria for stepsize control in the program. All of the timing results have been obtained without any attempt to optimize coding or procedures. Hence, it is concluded that the rational approximation methods are fast and accurate integration procedures and well-suited for the numerical solution of the equation of chemical kinetics.

## APPENDIX A

### SOLUTIONS FOR SPECIFIC INTEGRATION FORMULAS

If  $m$  is set equal to 1 in Eq. (3.6) the result is

$$(I-hA) c_1 = Ay_0 + b$$

so that solving for  $c_1$  we have

$$c_1 = (I-hA)^{-1} (Ay_0 + b)$$

Using this expression for  $c_1$  in Eq. (3.2) with  $t = h$  we obtain formula (3.8)

$$\bar{y}(h) = y_0 + (I-hA)^{-1} (Ay_0 + b) h = (I-hA)^{-1} (y_0 + hb)$$

When  $m = 1$ , Eq. (3.7) reduces to

$$(I - \frac{1}{2} hA) c_1 = Ay_0 + b$$

and replacing  $h$  by  $\frac{1}{2} h$  in the preceding equation, we immediately have Eq. (3.10)

$$\bar{y}(h) = y_0 + (I - \frac{1}{2} hA)^{-1} (Ay_0 + b) h = (I - \frac{1}{2} hA)^{-1} [(I + \frac{1}{2} hA)y_0 + hb]$$

Setting  $m = 2$  in (3.6) results in the following two equations

$$(I - \frac{1}{2} hA) c_1 + (hI - \frac{1}{4} h^2 A) c_2 = Ay_0 + b$$

$$(I - hA) c_1 + (2hI - h^2 A) c_2 = Ay_0 + b$$

Subtracting the second equation from twice the first equation yields

$$c_1 = -\frac{1}{2} h^2 A c_2 + Ay_0 + b$$

Substituting this expression for  $c_1$  into the second equation gives

$$c_2 = \left[ I - \frac{3}{4} hA + \frac{1}{4} (hA)^2 \right]^{-1} \frac{1}{2} A (Ay_0 + b)$$

Substituting this expression for  $c_2$  into the equation for  $c_1$

$$\begin{aligned} c_1 &= -\frac{1}{2} h^2 A \left[ I - \frac{3}{4} hA + \frac{1}{4} (hA)^2 \right]^{-1} \frac{1}{2} A (Ay_0 + b) + Ay_0 + b \\ &= \left[ I - \frac{3}{4} hA + \frac{1}{4} (hA)^2 \right]^{-1} \left[ -\frac{1}{4} (hA)^2 + I - \frac{3}{4} hA + \frac{1}{4} (hA)^2 \right] (Ay_0 + b) \\ &= \left[ I - \frac{3}{4} hA + \frac{1}{4} (hA)^2 \right]^{-1} \left[ I - \frac{3}{4} hA \right] \left[ Ay_0 + b \right] \end{aligned}$$

The result of placing these expressions for  $c_1$  and  $c_2$  into Eq. (3.2) is Eq. (3.9);

$$\bar{y}(h) = \left[ I - \frac{3}{4} hA + \frac{1}{4} (hA)^2 \right]^{-1} \left[ (I + \frac{1}{4} hA) y_0 + (I - \frac{1}{4} hA) hb \right]$$

Equation (3.7) yields the following equations when  $m = 2$

$$(I - \frac{1}{4} hA) c_1 + (\frac{1}{2} hI - \frac{1}{12} h^2 A) c_2 = Ay_0 + b$$

$$(I - \frac{1}{2} hA) c_1 + (hI - \frac{1}{3} h^2 A) c_2 = Ay_0 + b$$

Subtracting the second equation from twice the first equation gives

$$c_1 = -\frac{1}{6} h^2 A c_2 + Ay_0 + b$$

Replacing  $c_1$  in the second equation by this expression we have

$$c_2 = \left[ I - \frac{1}{2} hA + \frac{1}{12} (hA)^2 \right]^{-1} \frac{1}{2} A(Ay_0 + b)$$

The above expressions for  $c_1$  and  $c_2$  may now be used in Eq. (3.2) to obtain Eq. (3.11)

$$\bar{y}(h) = \left[ I - \frac{1}{2} hA + \frac{1}{12} (hA)^2 \right]^{-1} \left[ \left( I + \frac{1}{2} hA + \frac{1}{12} (hA)^2 \right) y_0 + hb \right]$$

In the above derivations, matrix polynomials with arguments involving the same matrix commute.



## APPENDIX B

### HYDROGEN-AIR CHEMISTRY

#### Reactions

- |                                      |                                       |
|--------------------------------------|---------------------------------------|
| 1. $H + O_2 \rightarrow OH + O$      | 9. $OH + O \rightarrow H + O_2$       |
| 2. $O + H_2 \rightarrow OH + H$      | 10. $OH + H \rightarrow O + H_2$      |
| 3. $H_2 + OH \rightarrow H + H_2O$   | 11. $H + H_2O \rightarrow H_2 + OH$   |
| 4. $2OH \rightarrow O + H_2O$        | 12. $O + H_2O \rightarrow 2OH$        |
| 5. $H_2 + X \rightarrow 2H + X$      | 13. $2H + X \rightarrow H_2 + X$      |
| 6. $H_2O + X \rightarrow OH + H + X$ | 14. $OH + H + X \rightarrow H_2O + X$ |
| 7. $OH + X \rightarrow O + H + X$    | 15. $O + H + X \rightarrow OH + X$    |
| 8. $O_2 + X \rightarrow 2O + X$      | 16. $2O + X \rightarrow O_2 + X$      |

X is a catalyst

#### Enthalpy Relationships

$$h_i = h_o + h_1 (T - T_R), \quad T_R = 2000^\circ K$$

<u>Species No.</u>	<u>Species Symbol</u>	<u>W</u>	<u><math>h_o</math></u>	<u><math>h_1</math></u>
1	H	1	60557.0	4.968
2	O	16	4255.9	0.31113
3	H <sub>2</sub> O	18	- 2245.8	0.67856
4	OH	17	1304.4	0.48735
5	O <sub>2</sub>	32	442.16	0.28216
6	H <sub>2</sub>	2	6325.5	4.0975
7	N <sub>2</sub>	28	480.0	0.3072

# DIFFERENTIAL EQUATIONS FOR THE HYDROGEN-AIR SYSTEM

$$\dot{Y}_1 = -R_1 + R_2 + R_3 + 2R_5 + R_6 + R_7 + R_9 - R_{10} - R_{11} - 2R_{13} - R_{14} - R_{15}$$

$$\dot{Y}_2 = R_1 - R_2 + R_4 + R_7 + 2R_8 - R_9 + R_{10} - R_{12} - R_{15} - 2R_{16}$$

$$\dot{Y}_3 = R_3 + R_4 - R_6 - R_{11} - R_{12} + R_{14}$$

$$\dot{Y}_4 = R_1 + R_2 - R_3 - 2R_4 + R_6 - R_7 - R_9 - R_{10} + R_{11} + 2R_{12} - R_{14} + R_{15}$$

$$\dot{Y}_5 = -R_1 - R_8 + R_9 + R_{16}$$

$$\dot{Y}_6 = -R_2 - R_3 - R_5 + R_{10} + R_{11} + R_{13}$$

$$\dot{Y}_7 = 0$$

where

$$R_1 = k_1 \rho Y_1 Y_5$$

$$R_9 = k_9 \rho Y_2 Y_4$$

$$R_2 = k_2 \rho Y_2 Y_6$$

$$R_{10} = k_{10} \rho Y_1 Y_4$$

$$R_3 = k_3 \rho Y_4 Y_6$$

$$R_{11} = k_{11} \rho Y_1 Y_3$$

$$R_4 = k_4 \rho Y_4 Y_4$$

$$R_{12} = k_{12} \rho Y_2 Y_3$$

$$R_5 = k_5 \rho Y_5 \sum Y_i$$

$$R_{13} = k_{13} \rho^2 Y_1 Y_1 \sum Y_i$$

$$R_6 = k_6 \rho Y_3 \sum Y_i$$

$$R_{14} = k_{14} \rho^2 Y_1 Y_4 \sum Y_i$$

$$R_7 = k_7 \rho Y_4 \sum Y_i$$

$$R_{15} = k_{15} \rho^2 Y_1 Y_2 \sum Y_i$$

$$R_8 = k_8 \rho Y_5 \sum Y_i$$

$$R_{16} = k_{16} \rho^2 Y_2 Y_2 \sum Y_i$$

The species subscripts are defined by the ordering in the enthalpy table on page B-1.

# REACTION RATE COEFFICIENTS

$$k_i = a_i T^{b_i} \exp(-e_i/T)$$

For the Reactions on Page B-1

<u>Reaction No.</u>	<u>a</u>	<u>b</u>	<u>e</u>
1	$2.4 \times 10^{14}$	0.0	8429.794
2	$3.3 \times 10^{12}$	0.0	3593.357
3	$6.3 \times 10^{13}$	0.0	2969.300
4	$7.6 \times 10^{12}$	0.0	503.2713
5	$2.4 \times 10^{19}$	-0.86	51957.73
6	$1.2 \times 10^{23}$	-1.34	59399.60
7	$7.5 \times 10^{14}$	0.06	50976.35
8	$2.5 \times 10^{16}$	-0.5	59335.68
9	$3.2 \times 10^{11}$	0.47	50.32713
10	$1.4 \times 10^{12}$	0.0	2611.978
11	$2.4 \times 10^{14}$	0.0	10412.68
12	$6.9 \times 10^{13}$	0.0	8928.032
13	$2.0 \times 10^{18}$	-1.0	0.0
14	$2.3 \times 10^{21}$	-1.5	0.0
15	$3.0 \times 10^{14}$	0.0	0.0
16	$2.2 \times 10^{13}$	0.0	0.0

"A" MATRIX IN EQUATION (3.1) FOR HYDROGEN-AIR CHEMISTRY

$$a_{11} = -k_1 \rho y_5 - k_{10} \rho y_4 - k_{11} \rho y_3 - 4k_{13} \rho^2 y_1 \Sigma y_i - k_{14} \rho^2 y_4 \Sigma y_i - k_{15} \rho^2 y_2 \Sigma y_i$$

$$a_{12} = k_2 \rho y_5 + k_9 \rho y_4 - k_{15} \rho^2 y_1 \Sigma y_i$$

$$a_{13} = k_6 \rho \Sigma y_i - k_{11} \rho y_1$$

$$a_{14} = k_3 \rho y_5 + k_7 \rho \Sigma y_i + k_9 \rho y_2 - k_{10} \rho y_1 - k_{14} \rho^2 y_1 \Sigma y_i$$

$$a_{15} = -k_1 \rho y_1$$

$$a_{16} = k_2 \rho y_2 + k_3 \rho y_4 + 2k_5 \rho \Sigma y_i$$

$$a_{21} = k_1 \rho y_5 + k_{10} \rho y_4 - k_{15} \rho^2 y_2 \Sigma y_i$$

$$a_{22} = -k_2 \rho y_5 - k_9 \rho y_4 - k_{12} \rho y_3 - k_{15} \rho^2 y_1 \Sigma y_i - 4k_{16} \rho^2 y_2 \Sigma y_i$$

$$a_{23} = -k_{12} \rho y_2$$

$$a_{24} = 2k_4 \rho y_4 + k_2 \rho \Sigma y_i - k_9 \rho y_2 + k_{10} \rho y_1$$

$$a_{25} = k_1 \rho y_1 + 2k_8 \rho \Sigma y_i$$

$$a_{26} = -k_2 \rho y_2$$

$$a_{31} = -k_{11} \rho y_3 + k_{14} \rho^2 y_4 \Sigma y_i$$

$$a_{32} = -k_{12} \rho y_3$$

$$a_{33} = -k_6 \rho \Sigma y_i - k_{12} \rho y_2 - k_{11} \rho y_1$$

$$a_{34} = k_3 \rho y_5 + 2k_4 \rho y_4 + k_{14} \rho^2 y_1 \Sigma y_i$$

$$a_{35} = 0$$

$$a_{36} = k_3 \rho y_4$$

$$a_{41} = k_1 \rho y_5 - k_{10} \rho y_4 + k_{11} \rho y_3 - k_{14} \rho^2 y_4 \Sigma y_i + k_{15} \rho^2 y_2 \Sigma y_i$$

$$a_{42} = k_2 \rho y_5 - k_9 \rho y_4 + 2k_{12} \rho y_3 + k_{15} \rho^2 y_1 \Sigma y_i$$

$$a_{43} = k_6 \rho \Sigma y_i + k_{11} \rho y_1 + 2k_{12} \rho y_2$$

$$a_{44} = -k_3 \rho y_5 - 4k_4 \rho y_4 - k_7 \rho \Sigma y_i - k_8 \rho y_2 - k_{10} \rho y_1 - k_{14} \rho^2 y_1 \Sigma y_i$$

$$a_{45} = k_1 \rho y_1$$

$$a_{46} = k_2 \rho y_2 - k_3 \rho y_4$$

$$a_{51} = -k_1 \rho y_5$$

$$a_{52} = k_9 \rho y_4 + 2k_{15} \rho^2 y_2 \Sigma y_i$$

$$a_{53} = 0$$

$$a_{54} = k_9 \rho y_2$$

$$a_{55} = -k_1 \rho y_1 - k_8 \rho \Sigma y_i$$

$$a_{56} = 0$$

$$a_{61} = k_{11} \rho y_3 + 2k_{12} \rho^2 y_1 \Sigma y_i + k_{10} \rho y_4$$

$$a_{62} = -k_2 \rho y_5$$

$$a_{63} = k_{11} \rho y_1$$

$$a_{64} = -k_3 \rho y_5 + k_{10} \rho y_1$$

$$a_{65} = 0$$

$$a_{66} = -k_2 \rho y_2 - k_3 \rho y_4 - k_8 \rho \Sigma y_i$$

## AIR CHEMISTRY

### Reactions

- |                                     |                                      |
|-------------------------------------|--------------------------------------|
| 1. $O_2 + O_2 \rightarrow 2O + O_2$ | 12. $2O + O_2 \rightarrow O_2 + O_2$ |
| 2. $O_2 + O \rightarrow 2O + O$     | 13. $2O + O \rightarrow O_2 + O$     |
| 3. $O_2 + X \rightarrow 2O + X$     | 14. $2O + X \rightarrow O_2 + X$     |
| 4. $N_2 + N_2 \rightarrow 2N + N_2$ | 15. $2N + N_2 \rightarrow N_2 + N_2$ |
| 5. $N_2 + N \rightarrow 2N + N$     | 16. $2N + N \rightarrow N_2 + N$     |
| 6. $N_2 + X \rightarrow 2N + X$     | 17. $2N + X \rightarrow N_2 + X$     |
| 7. $NO + X \rightarrow N + O + X$   | 18. $N + O + X \rightarrow NO + X$   |
| 8. $O + N_2 \rightarrow NO + N$     | 19. $NO + N \rightarrow O + N_2$     |
| 9. $NO + O \rightarrow N + O_2$     | 20. $N + O_2 \rightarrow NO + O$     |
| 10. $N_2 + O_2 \rightarrow 2NO$     | 21. $2NO \rightarrow N_2 + O_2$      |
| 11. $N + O \rightarrow NO^+ + e^-$  | 22. $NO^+ + e^- \rightarrow N + O$   |

X is a catalyst

# ENTHALPY RELATIONSHIPS

$$h_i = h_o + h_1 T + h_2 T^2$$

52

Species No.	Species Symbol	W	Temp. Range	$h_o$	$h_1$	$h_2$
1	O	16.0	100-500 500-3000 3000-6000	1.6604x10 <sup>8</sup> 1.6655x10 <sup>8</sup> 1.6826x10 <sup>8</sup>	1.6198x10 <sup>4</sup> 1.4153x10 <sup>4</sup> 1.3014x10 <sup>4</sup>	-2.0688 -2.3937x10 <sup>-2</sup> 1.6602x10 <sup>-1</sup>
2	N	14.008	100-2800 2800-4400 4400-6000	3.6200x10 <sup>8</sup> 3.6446x10 <sup>8</sup> 3.7390x10 <sup>8</sup>	1.5968x10 <sup>4</sup> 1.4211x10 <sup>4</sup> 9.9185x10 <sup>3</sup>	8.6900x10 <sup>-3</sup> 3.2240x10 <sup>-1</sup> 8.1015x10 <sup>-1</sup>
3	NO	30.008	100-2000 2000-3600 3600-6000	3.2270x10 <sup>7</sup> 2.9632x10 <sup>7</sup> 3.0281x10 <sup>7</sup>	1.0656x10 <sup>4</sup> 1.3295x10 <sup>4</sup> 1.2934x10 <sup>4</sup>	6.8605x10 <sup>-1</sup> 2.6333x10 <sup>-2</sup> 7.6468x10 <sup>-2</sup>
4	NO <sup>+</sup>	30.008	100-500 500-1600 1600-6000	3.5418x10 <sup>8</sup> 3.5439x10 <sup>8</sup> 3.5211x10 <sup>8</sup>	1.0377x10 <sup>4</sup> 9.5492x10 <sup>3</sup> 1.2405x10 <sup>4</sup>	1.9102x10 <sup>-1</sup> 1.0191 1.2662x10 <sup>-1</sup>
5	e <sup>-</sup>	5.4862x10 <sup>-4</sup>	100-6000	0.0	4.08105x10 <sup>8</sup>	0.0
6	O <sub>2</sub>	32.0	100-1000 1000-3200 3200-6000	7.5222x10 <sup>4</sup> -8.3866x10 <sup>5</sup> -3.4512x10 <sup>6</sup>	9.1557x10 <sup>3</sup> 1.0983x10 <sup>4</sup> 1.2616x10 <sup>4</sup>	1.3333 4.1981x10 <sup>-1</sup> 1.6427x10 <sup>-1</sup>
7	N <sub>2</sub>	28.016	100-2000 2000-3200 3200-6000	9.7150x10 <sup>3</sup> -2.9585x10 <sup>6</sup> -2.6350x10 <sup>6</sup>	1.0841x10 <sup>4</sup> 1.3809x10 <sup>4</sup> 1.3607x10 <sup>4</sup>	8.0879x10 <sup>-1</sup> 6.6742x10 <sup>-2</sup> 9.8333x10 <sup>-2</sup>

# DIFFERENTIAL EQUATIONS FOR DISSOCIATING AIR

1.  $\dot{Y}_1 = 2R_1 + 2R_2 + 2R_3 + R_7 + R_{19} + R_{20} + R_{22}$   
 $- R_8 - R_9 - R_{11} - 2R_{12} - 2R_{13} - 2R_{14} - R_{18}$
2.  $\dot{Y}_2 = 2R_4 + 2R_5 + 2R_6 + R_7 + R_8 + R_9 + R_{22}$   
 $- R_{11} - 2R_{15} - 2R_{16} - 2R_{17} - R_{18} - R_{19} - R_{20}$
3.  $\dot{Y}_3 = R_8 + 2R_{10} + R_{18} + R_{20} - R_7 - R_9 - R_{19} - 2R_{21}$
4.  $\dot{Y}_4 = R_{11} - R_{22}$
5.  $\dot{Y}_5 = R_{11} - R_{22}$
6.  $\dot{Y}_6 = R_9 + R_{12} + R_{13} + R_{14} + R_{21} - R_1 - R_2 - R_3 - R_{10} - R_{20}$
7.  $\dot{Y}_7 = R_{15} + R_{16} + R_{17} + R_{19} + R_{21} - R_4 - R_5 - R_6 - R_8 - R_{10}$

where

$R_1 = k_1 \rho Y_6 Y_6$	$R_{12} = k_{12} \rho^2 Y_1 Y_1 Y_6$
$R_2 = k_2 \rho Y_1 Y_6$	$R_{13} = k_{13} \rho^2 Y_1 Y_1 Y_1$
$R_3 = k_3 \rho Y_6 \sum_{i \neq 1,6} Y_i$	$R_{14} = k_{14} \rho^2 Y_1 Y_1 \sum_{i \neq 1,6} Y_i$
$R_4 = k_4 \rho Y_7 Y_7$	$R_{15} = k_{15} \rho^2 Y_2 Y_2 Y_7$
$R_5 = k_5 \rho Y_2 Y_7$	$R_{16} = k_{16} \rho^2 Y_2 Y_2 Y_2$
$R_6 = k_6 \rho Y_7 \sum_{i \neq 2,7} Y_i$	$R_{17} = k_{17} \rho^2 Y_2 Y_2 \sum_{i \neq 2,7} Y_i$
$R_7 = k_7 \rho Y_3 \sum Y_i$	$R_{18} = k_{18} \rho^2 Y_1 Y_2 \sum Y_i$
$R_8 = k_8 \rho Y_1 Y_7$	$R_{19} = k_{19} \rho Y_2 Y_3$
$R_9 = k_9 \rho Y_1 Y_3$	$R_{20} = k_{20} \rho Y_2 Y_6$
$R_{10} = k_{10} \rho Y_6 Y_7$	$R_{21} = k_{21} \rho Y_3 Y_3$
$R_{11} = k_{11} \rho Y_1 Y_2$	$R_{22} = k_{22} \rho Y_4 Y_5$

The species subscripts are defined by the ordering in the enthalpy table on page B-7.



# REACTION RATE COEFFICIENTS

$$k_i = a_i T^{b_i} \exp(-e_i/T)$$

For the reactions on page B-6

	<u>a</u>	<u>b</u>	<u>e</u>
1.	$2.3 \times 10^{19}$	-1.0	59400
2.	$8.5 \times 10^{19}$	-1.0	59400
3.	$3.0 \times 10^{18}$	-1.0	59400
4.	$3.8 \times 10^{19}$	-1.0	113200
5.	$1.3 \times 10^{20}$	-1.0	113200
6.	$1.9 \times 10^{19}$	-1.0	113200
7.	$2.4 \times 10^{17}$	-0.5	75500
8.	$6.8 \times 10^{13}$	0.0	37750
9.	$4.3 \times 10^7$	1.5	19100
10.	$2.0 \times 10^{14}$	0.0	61600
11.	$1.3 \times 10^8$	1.0	31900
12.	$1.9 \times 10^{16}$	-0.5	0
13.	$7.1 \times 10^{16}$	-0.5	0
14.	$2.5 \times 10^{15}$	-0.5	0
15.	$2.0 \times 10^{18}$	-1.0	0
16.	$7.0 \times 10^{18}$	-1.0	0
17.	$1.0 \times 10^{18}$	-1.0	0
18.	$6.0 \times 10^{16}$	-0.5	0
19.	$1.5 \times 10^{13}$	0.0	0
20.	$1.8 \times 10^8$	1.5	3020
21.	$1.0 \times 10^{13}$	0.0	40000
22.	$2.0 \times 10^{19}$	-1.0	0

"A" MATRIX IN EQUATION (3.1) FOR DISSOCIATING AIR CHEMISTRY

$$a_{11} = 2k_2 \rho Y_6 + k_7 \rho Y_3 - k_8 \rho Y_7 - k_9 \rho Y_3 - k_{11} \rho Y_2 - 4k_{12} \rho^2 Y_1 Y_6 \\ - 6k_{13} \rho^2 Y_1 Y_1 - 4k_{14} \rho^2 Y_1 \sum_{i \neq 1,6} Y_i - k_{18} \rho^2 Y_2 \sum Y_i - k_{18} \rho^2 Y_1 Y_2$$

$$a_{12} = 2k_3 \rho Y_6 + k_7 \rho Y_3 + k_{19} \rho Y_3 + k_{20} \rho Y_6 - k_{11} \rho Y_1 - 2k_{14} \rho^2 Y_1 Y_1 \\ - k_{18} \rho^2 Y_1 \sum Y_i - k_{18} \rho^2 Y_1 Y_2$$

$$a_{13} = 2k_3 \rho Y_6 + k_7 \rho \sum Y_i + k_7 \rho Y_3 + k_{19} \rho Y_2 - k_9 \rho Y_1 - 2k_{14} \rho^2 Y_1 Y_1 - k_{18} \rho^2 Y_1 Y_2$$

$$a_{14} = 2k_3 \rho Y_6 + k_7 \rho Y_3 + k_{22} \rho Y_6 - 2k_{14} \rho^2 Y_1 Y_1 - k_{18} \rho^2 Y_1 Y_2$$

$$a_{15} = 2k_3 \rho Y_6 + k_7 \rho Y_3 + k_{22} \rho Y_4 - 2k_{14} \rho^2 Y_1 Y_1 - k_{18} \rho^2 Y_1 Y_2$$

$$a_{16} = 4k_1 \rho Y_6 + 2k_2 \rho Y_1 + 2k_3 \rho \sum_{i \neq 1,6} Y_i + k_7 \rho Y_3 + k_{20} \rho Y_2 - 2k_{12} \rho^2 Y_1 Y_1 \\ - k_{18} \rho^2 Y_1 Y_2$$

$$a_{17} = 2k_3 \rho Y_6 + k_7 \rho Y_3 - k_8 \rho Y_1 - 2k_{14} \rho^2 Y_1 Y_1 - k_{18} \rho^2 Y_1 Y_2$$

$$a_{21} = 2k_6 \rho Y_7 + k_7 \rho Y_3 + k_8 \rho Y_7 + k_9 \rho Y_3 - k_{11} \rho Y_2 - 2k_{17} \rho^2 Y_2 Y_2 \\ - k_{18} \rho^2 Y_2 \sum Y_i - k_{18} \rho^2 Y_1 Y_2$$

$$a_{22} = 2k_6 \rho Y_7 + k_7 \rho Y_3 - k_{11} \rho Y_1 - 4k_{15} \rho^2 Y_2 Y_7 - 6k_{16} \rho^2 Y_2 Y_2 \\ - 4k_{17} \rho^2 Y_2 \sum_{i \neq 2,7} Y_i - k_{18} \rho^2 Y_1 \sum Y_i - k_{18} \rho^2 Y_1 Y_2 - k_{19} \rho Y_3 - k_{20} \rho Y_6$$

$$a_{23} = 2k_6 \rho Y_7 + k_7 \rho \sum Y_i + k_7 \rho Y_3 + k_9 \rho Y_1 - 2k_{17} \rho^2 Y_2 Y_2 - k_{18} \rho^2 Y_1 Y_2 - k_{19} \rho Y_2$$

$$a_{24} = 2k_6 \rho Y_7 + k_7 \rho Y_3 + k_{22} \rho Y_6 - 2k_{17} \rho^2 Y_2 Y_2 - k_{18} \rho^2 Y_1 Y_2$$

$$a_{25} = 2k_6 \rho Y_7 + k_7 \rho Y_3 + k_{22} \rho Y_4 - 2k_{17} \rho^2 Y_2 Y_2 - k_{18} \rho^2 Y_1 Y_2$$

$$a_{26} = 2k_6 \rho Y_7 + k_7 \rho Y_3 - 2k_{17} \rho^2 Y_2 Y_2 - k_{18} \rho^2 Y_1 Y_2 - k_{20} \rho Y_2$$

$$a_{27} = 4k_4 \rho Y_7 + 2k_5 \rho Y_2 + 2k_6 \rho \sum_{i \neq 2,7} Y_i + k_7 \rho Y_3 + k_8 \rho Y_1 - 2k_{15} \rho^2 Y_2 Y_2 \\ - k_{18} \rho^2 Y_1 Y_2$$

$$\begin{aligned}
a_{31} &= k_8 \rho y_7 + k_{18} \rho^2 y_2 \sum y_i + k_{18} \rho^2 y_1 y_2 - k_7 \rho y_3 - k_9 \rho y_3 \\
a_{32} &= k_{18} \rho^2 y_1 \sum y_i + k_{18} \rho^2 y_1 y_2 + k_{20} \rho y_6 - k_7 \rho y_3 - k_{19} \rho y_3 \\
a_{33} &= k_{18} \rho^2 y_1 y_2 = k_7 \rho \sum y_i - k_7 \rho y_3 - k_9 \rho y_1 - k_{19} \rho y_2 - 4k_{21} \rho y_3 \\
a_{34} &= k_{18} \rho^2 y_1 y_2 - k_7 \rho y_3 \\
a_{35} &= k_{18} \rho^2 y_1 y_2 - k_7 \rho y_3 \\
a_{36} &= 2k_{10} \rho y_7 + k_{18} \rho^2 y_1 y_2 + k_{20} \rho y_2 - k_7 \rho y_3 \\
a_{37} &= k_8 \rho y_1 + 2k_{10} \rho y_6 + k_{18} \rho^2 y_1 y_2 - k_7 \rho y_3 \\
a_{41} &= k_{11} \rho y_2 & a_{51} &= k_{11} \rho y_2 \\
a_{42} &= k_{11} \rho y_1 & a_{52} &= k_{11} \rho y_1 \\
a_{43} &= 0 & a_{53} &= 0 \\
a_{44} &= -k_{22} \rho y_5 & a_{54} &= -k_{22} \rho y_5 \\
a_{45} &= -k_{22} \rho y_4 & a_{55} &= -k_{22} \rho y_4 \\
a_{46} &= 0 & a_{56} &= 0 \\
a_{47} &= 0 & a_{57} &= 0 \\
a_{61} &= k_9 \rho y_3 + 2k_{12} \rho^2 y_1 y_6 + 3k_{13} \rho^2 y_1 y_1 + 2k_{14} \rho y_1 \sum_{i \neq 1,6} y_i - k_2 \rho y_6 \\
a_{62} &= k_{14} \rho^2 y_1 y_1 - k_3 \rho y_6 - k_{20} \rho y_6 \\
a_{63} &= k_9 \rho y_1 + k_{14} \rho^2 y_1 y_1 + 2k_{21} \rho y_3 - k_3 \rho y_6 \\
a_{64} &= k_{14} \rho^2 y_1 y_1 - k_3 \rho y_6 \\
a_{65} &= k_{14} \rho^2 y_1 y_1 - k_3 \rho y_6 \\
a_{66} &= k_{12} \rho^2 y_1 y_1 - 2k_1 \rho y_6 - k_2 \rho y_1 - k_3 \rho \sum_{i \neq 1,6} y_i - k_{10} \rho y_7 - k_{20} \rho y_2 \\
a_{67} &= k_{14} \rho^2 y_1 y_1 - k_3 \rho y_6 - k_{10} \rho y_6 \\
a_{71} &= k_{17} \rho^2 y_2 y_2 - k_6 \rho y_7 - k_8 \rho y_7
\end{aligned}$$

$$a_{72} = 2k_{15} \rho^2 y_2 y_7 + 3k_{16} \rho^2 y_2 y_2 + 2k_{17} \rho^2 y_2 \sum_{i \neq 2,7} y_i + k_{18} \rho y_3 - k_5 \rho y_7$$

$$a_{73} = k_{17} \rho^2 y_2 y_2 + k_{18} \rho y_2 + 2k_{21} \rho y_3 - k_5 \rho y_7$$

$$a_{74} = k_{17} \rho^2 y_2 y_2 - k_5 \rho y_7$$

$$a_{75} = k_{17} \rho^2 y_2 y_2 - k_5 \rho y_7$$

$$a_{76} = k_{17} \rho^2 y_2 y_2 - k_5 \rho y_7 - k_{10} \rho y_7$$

$$a_{77} = k_{15} \rho^2 y_2 y_2 - 2k_4 \rho y_7 - k_5 \rho y_2 - k_5 \rho \sum_{i \neq 2,7} y_i + k_8 \rho y_1 - k_{10} \rho y_6$$

To obtain  $\partial \dot{y}_i / \partial T$  replace  $R_i$  in the expression for  $\dot{y}_i$  by  $(b_i/T + e_i/T^2)R_i$ .

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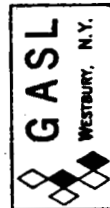
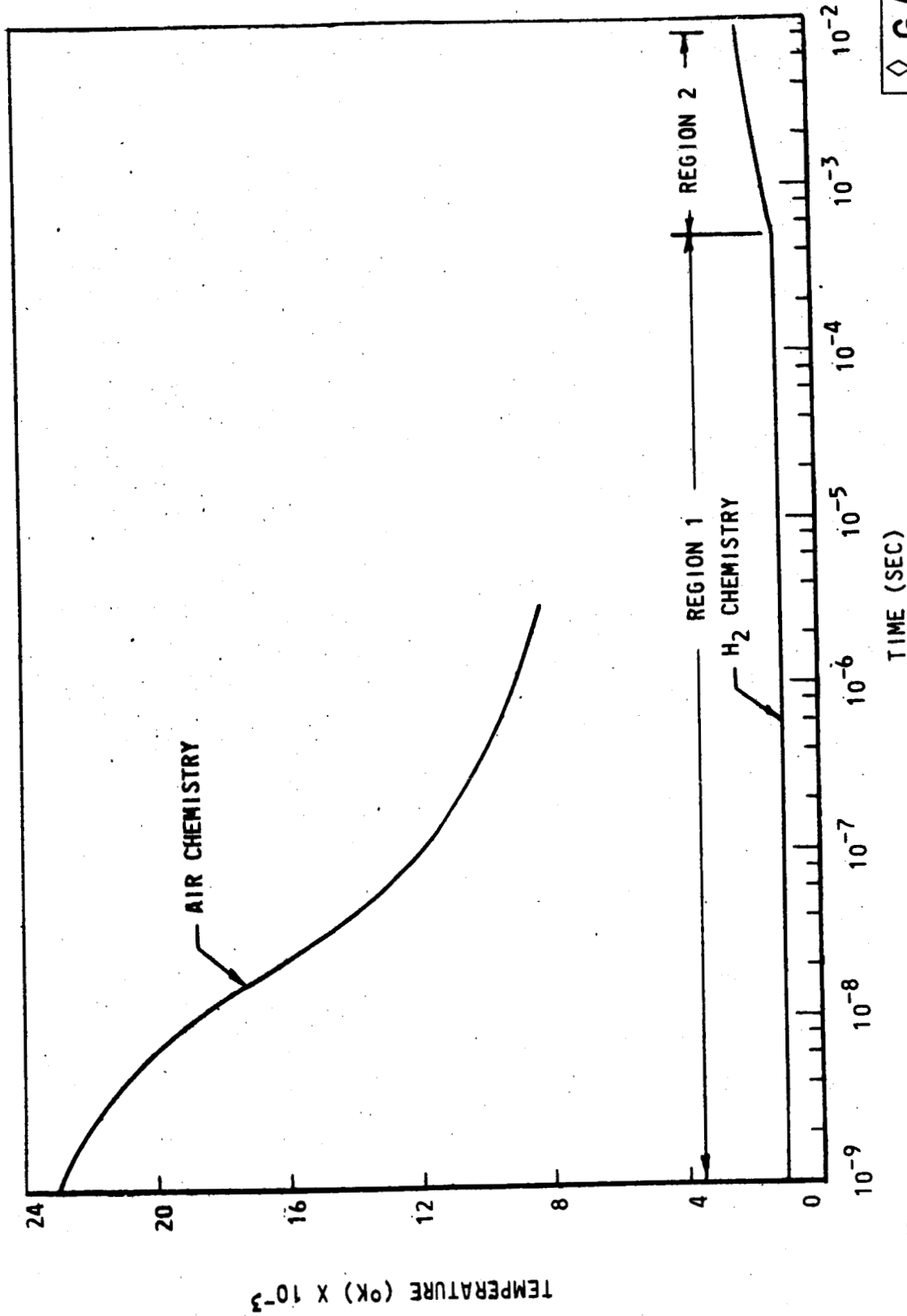


FIG. 1. COMPARISON OF TEMPERATURE VS. TIME FOR THE AIR CHEMISTRY AND HYDROGEN CHEMISTRY SYSTEMS

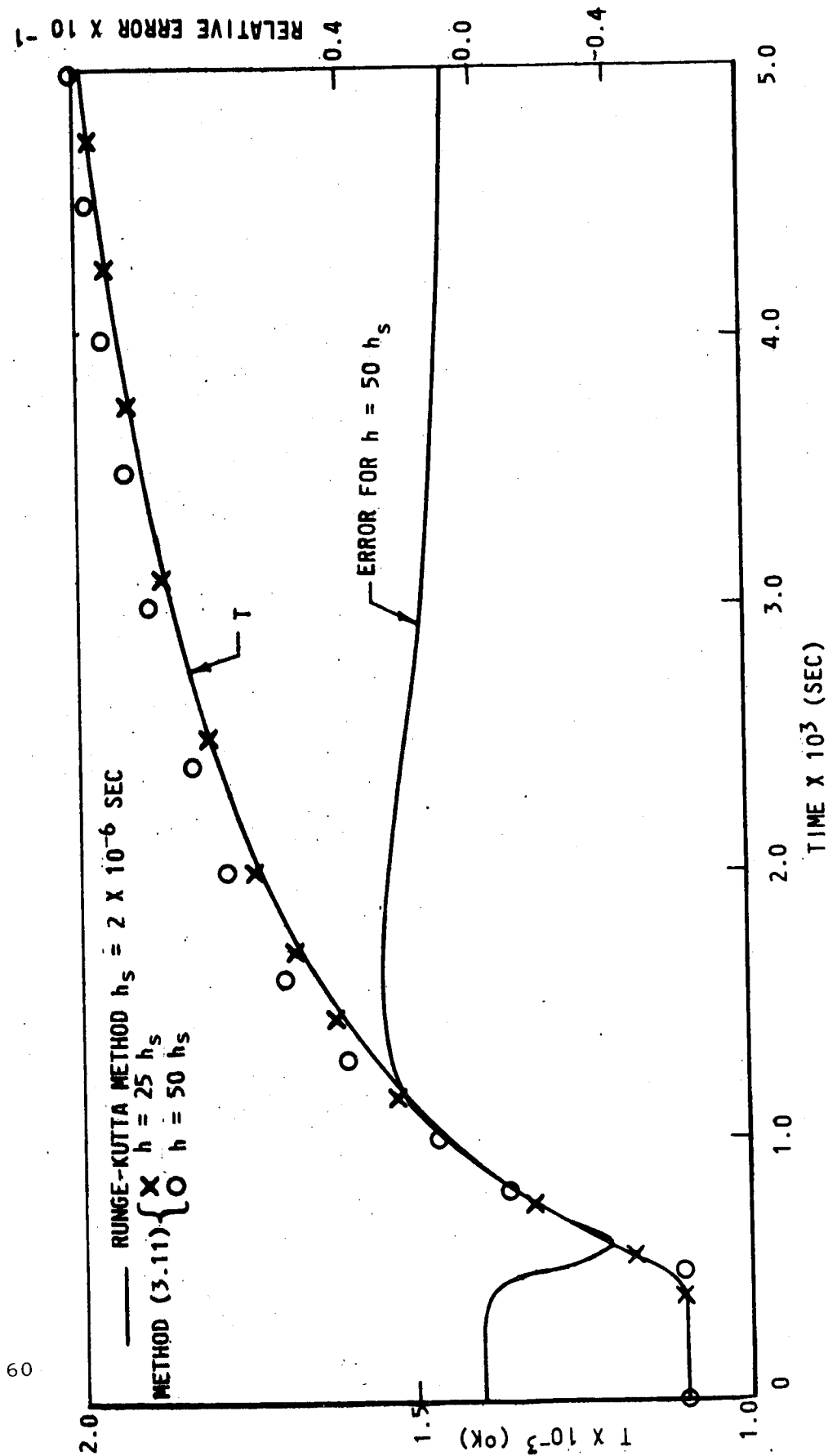


FIG 2. TEMPERATURE AND RELATIVE ERROR VS. TIME-HYDROGEN CHEMISTRY

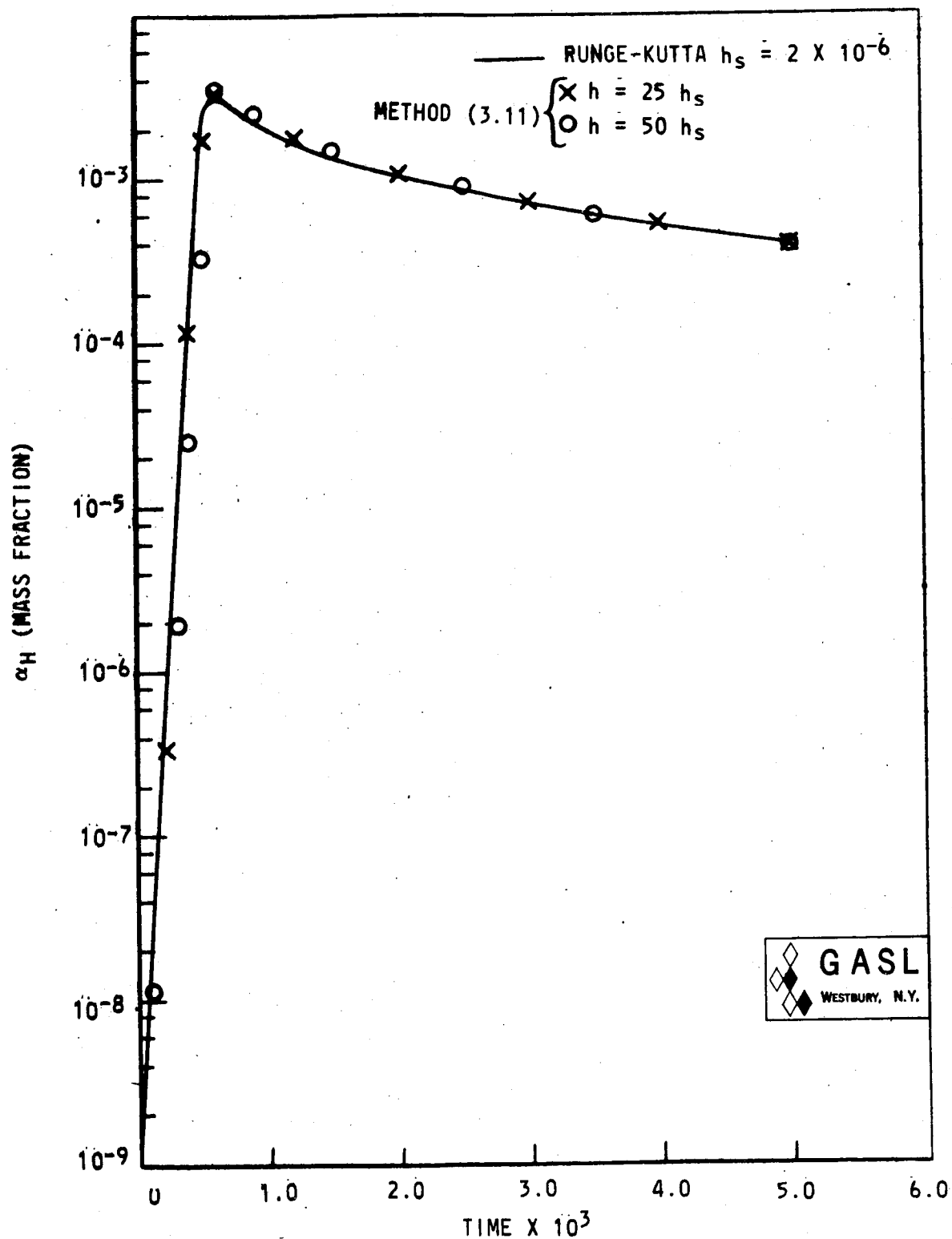


FIG. 3. MASS FRACTION  $\alpha_H$  VS. TIME



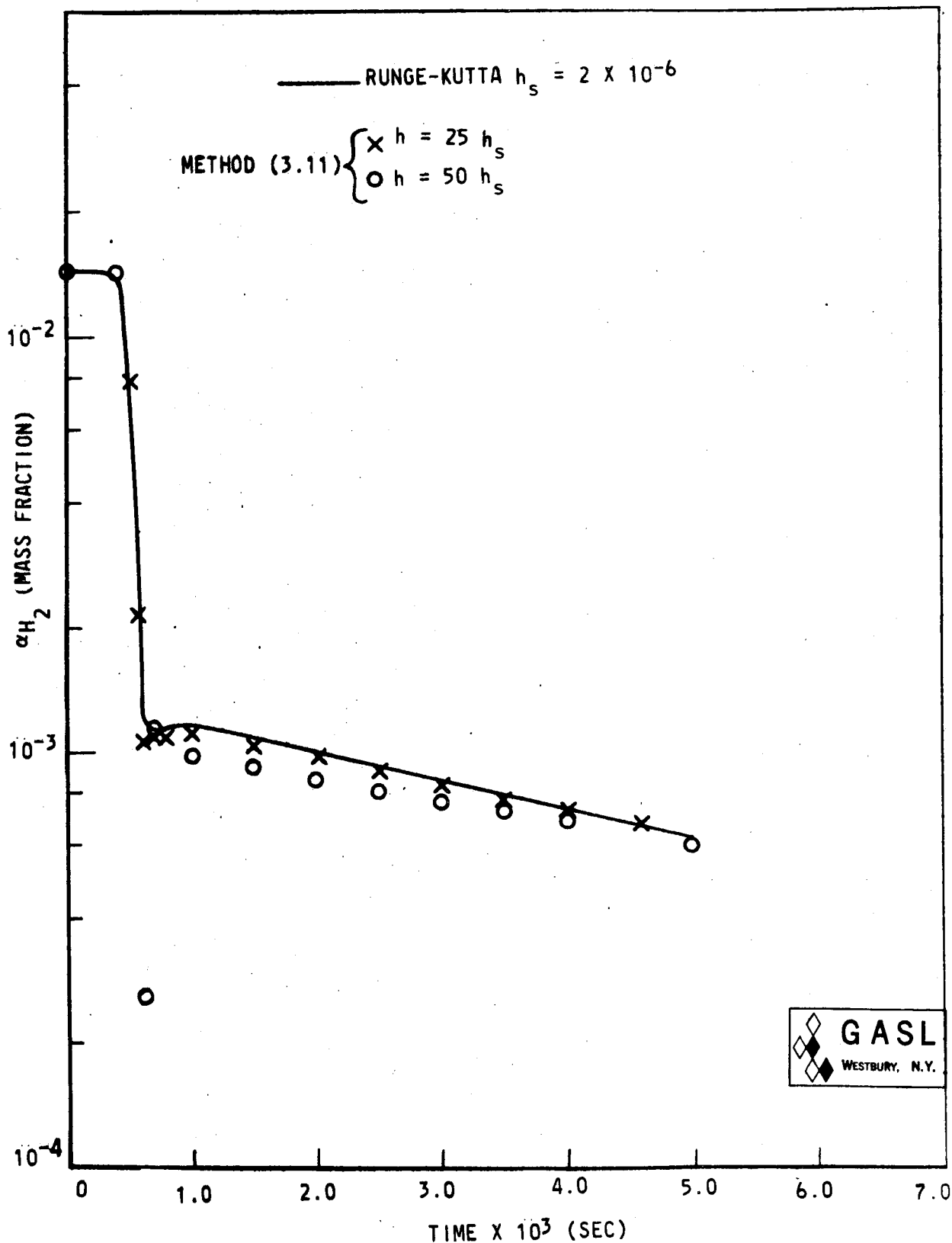


FIG. 4. MASS FRACTION  $\alpha_{H_2}$  VS. TIME

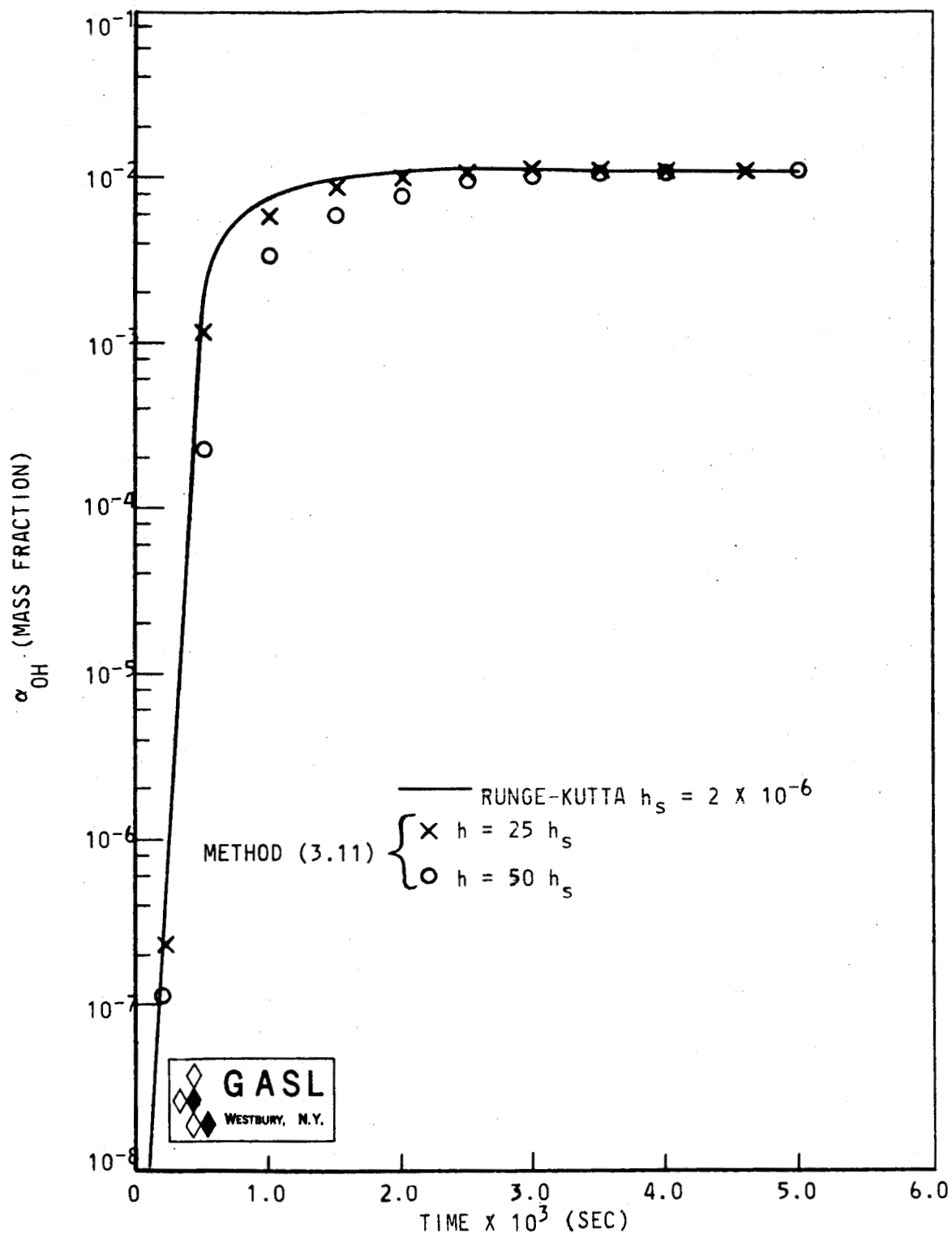


FIG. 5. MASS FRACTION  $\alpha_{OH}$  VS. TIME

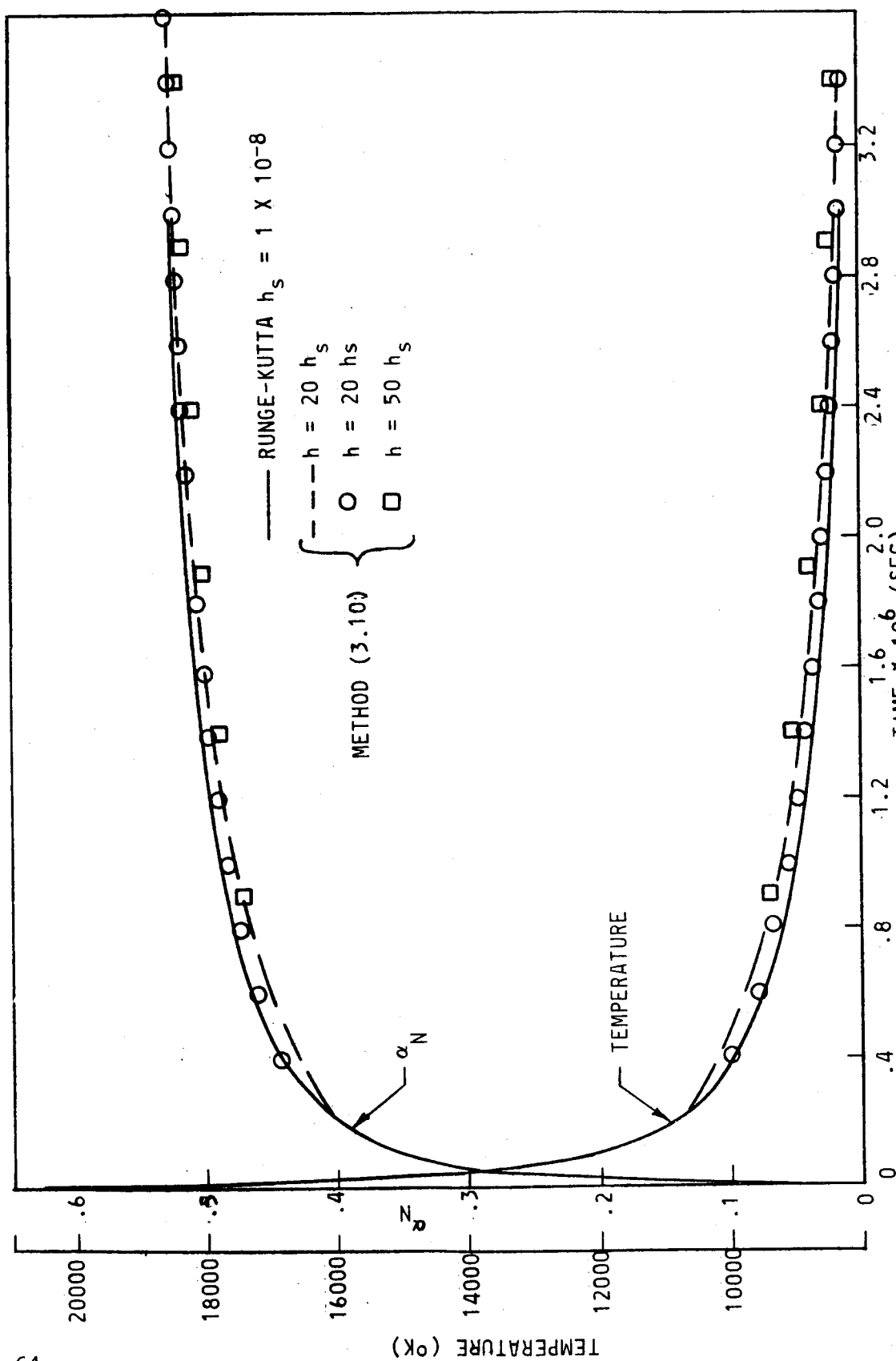


FIG. 6. TEMPERATURE AND MASS FRACTION  $\alpha_N$  VS. TIME-AIR CHEMISTRY

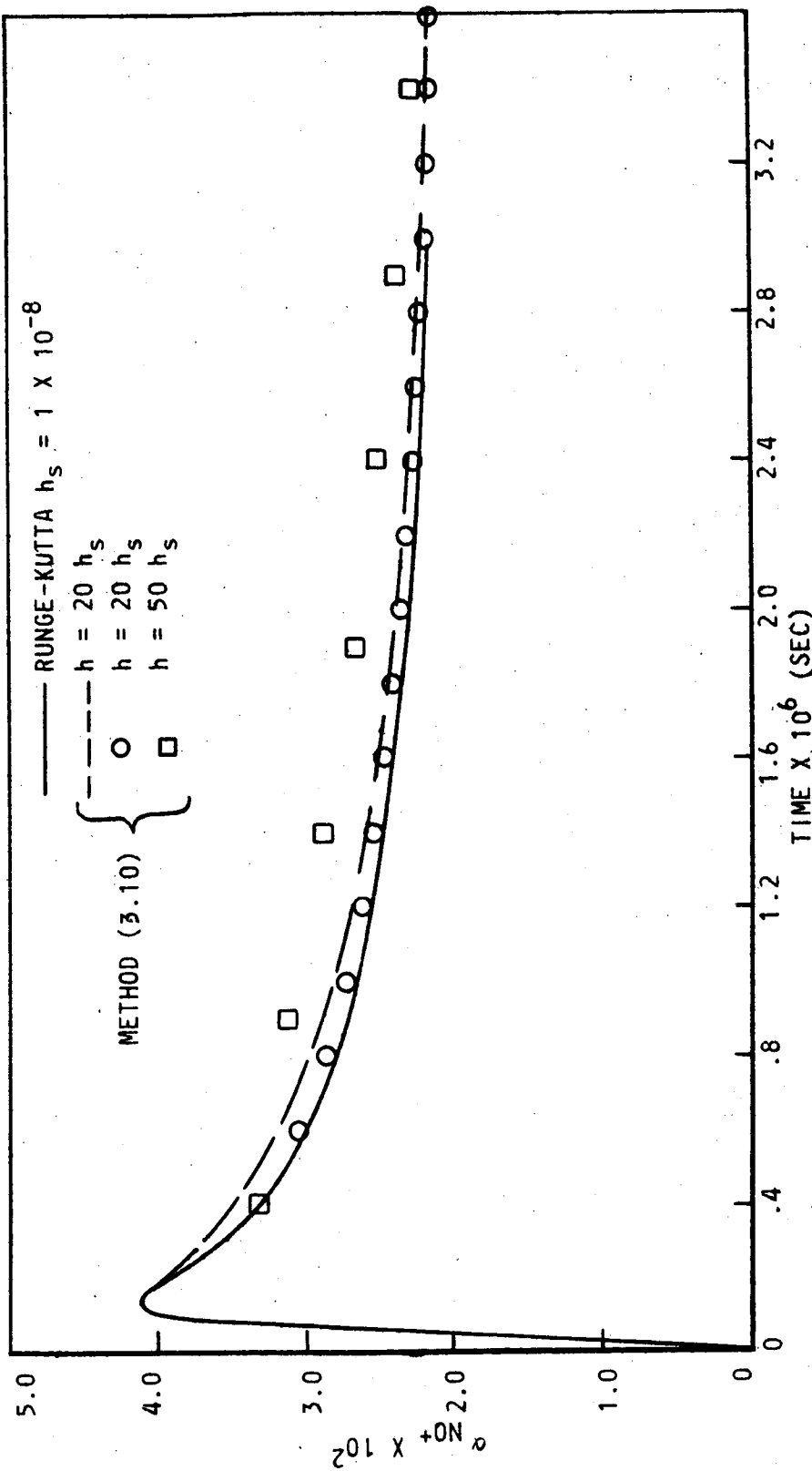


FIG. 7. MASS FRACTION  $\alpha_{NO^+}$  VS. TIME

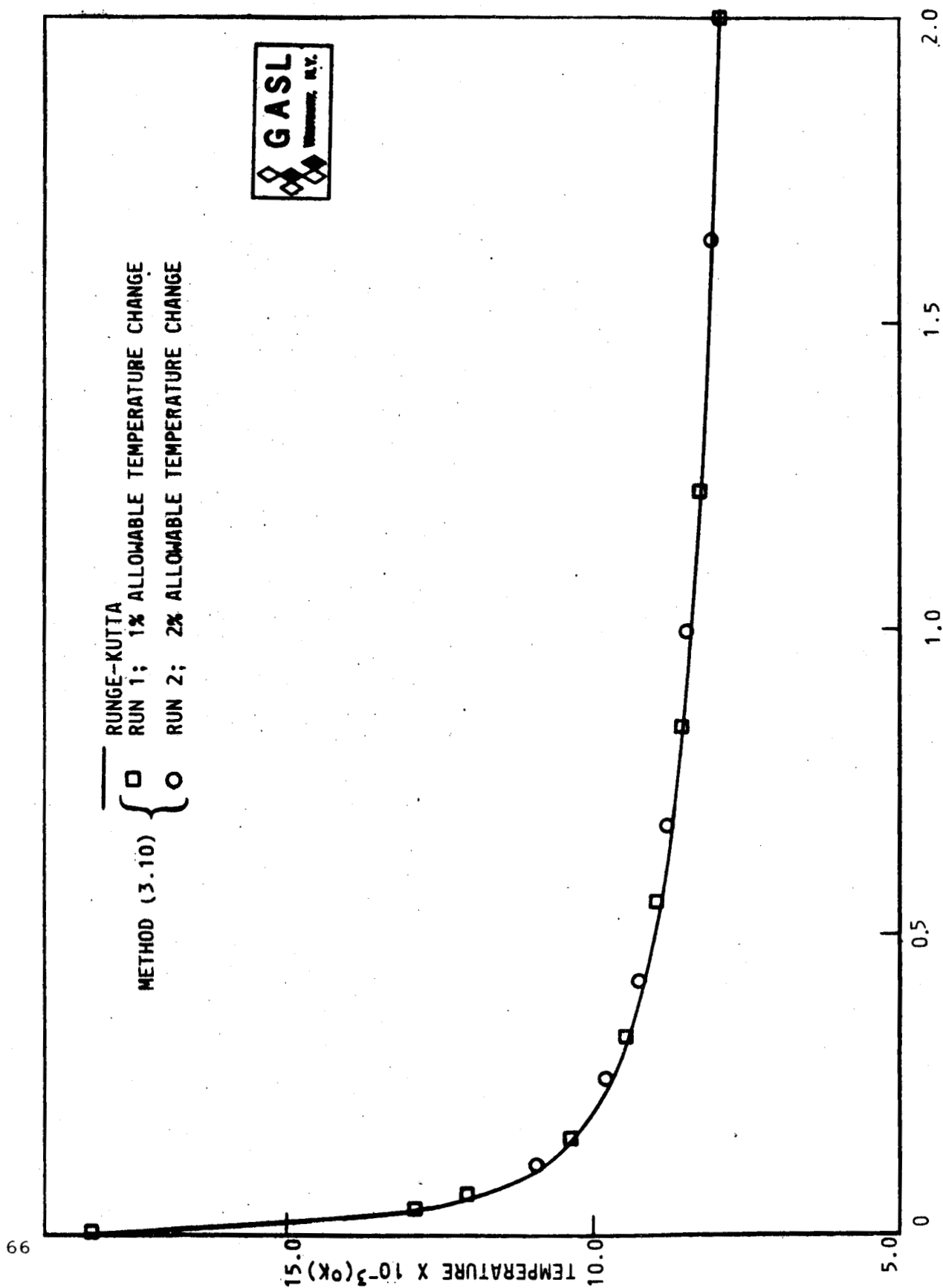


FIG. 8. TEMPERATURE VS. TIME - AIR CHEMISTRY WITH VARIABLE STEPSIZE

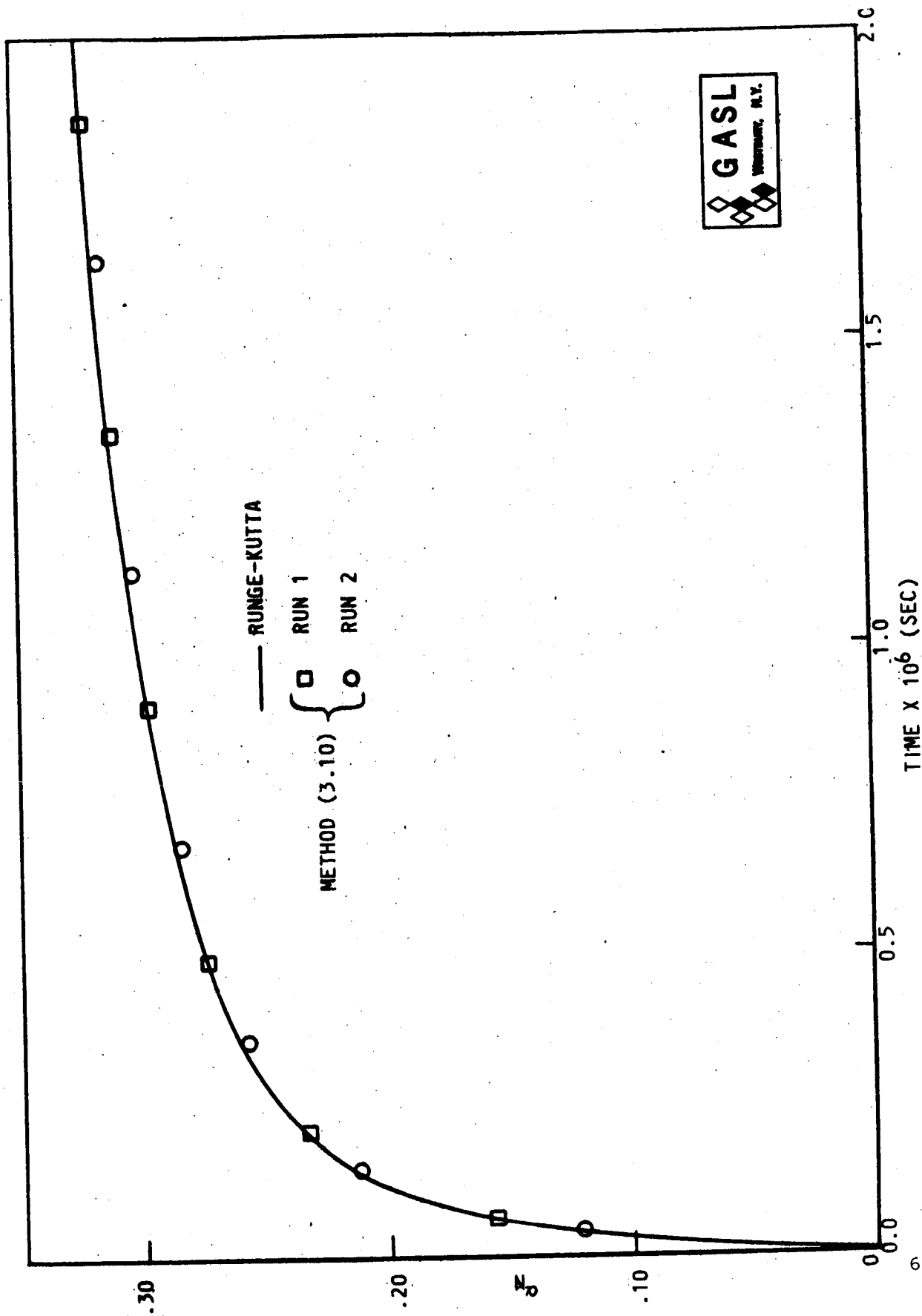


FIG. 9. MASS FRACTION  $\alpha_N$  VS. TIME - AIR CHEMISTRY  
 WITH VARIABLE STEP SIZE

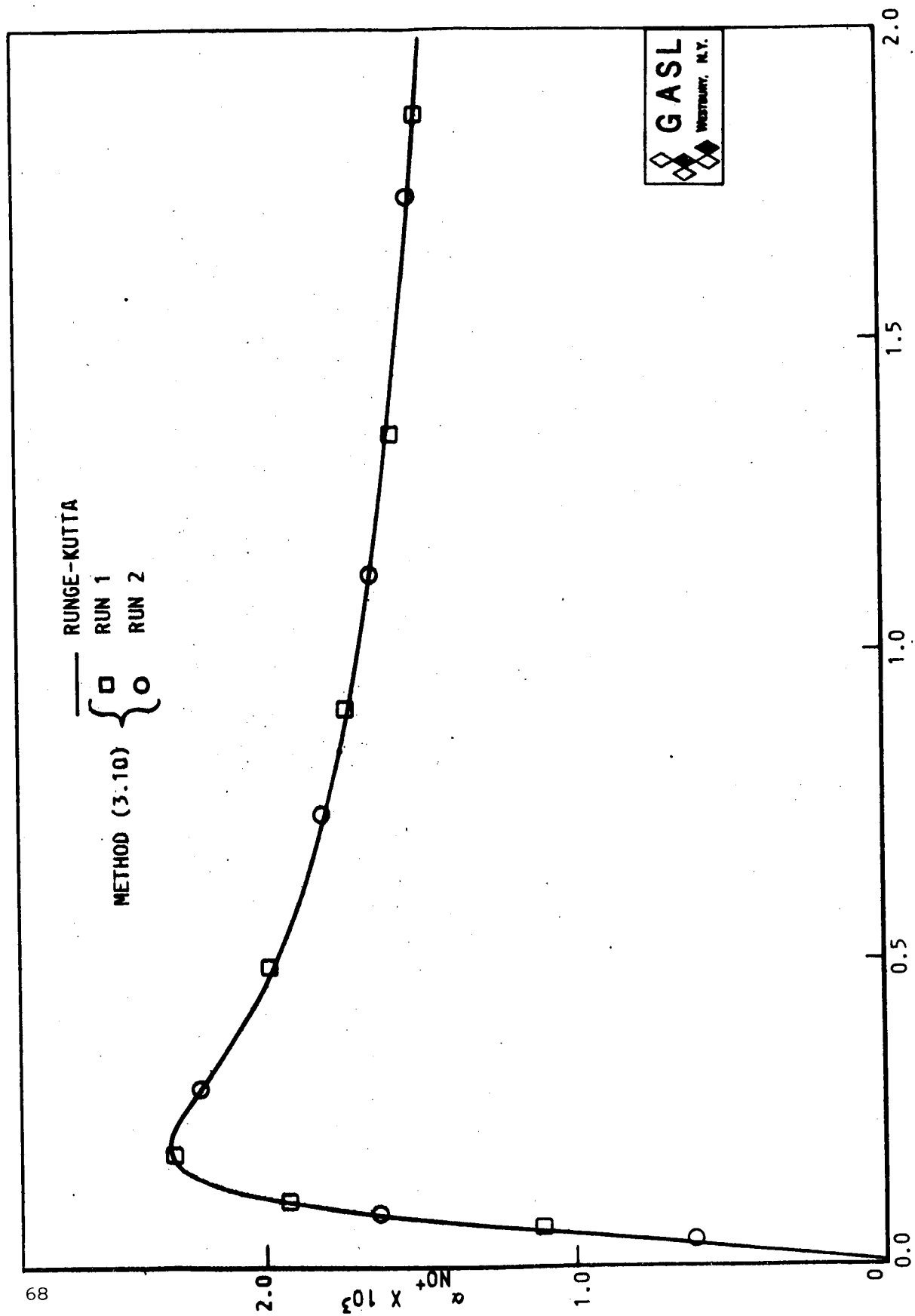


FIG. 10. MASS FRACTION  $\alpha_{NO^+}$  VS. TIME - AIR CHEMISTRY WITH VARIABLE STEPSIZE